# Synthesis and Characterization of High-Spin Organic Materials: Prototypes for the Polaronic Ferromagnet

Thesis by

**Michael Mark Murray**

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**Abstract**

The design, synthesis and magnetic characterization of thiophene-based models for the polaronic ferromagnet are described. Synthetic strategies employing Wittig and Suzuki coupling were employed to produce polymers with extended π-systems. Oxidative doping using $AsF_5$ or $I_2$ produces radical cations (polarons) that are stable at room temperature. Magnetic characterization of the doped polymers, using SQUID-based magnetometry, indicates that in several instances ferromagnetic coupling of polarons occurs along the polymer chain. An investigation of the influence of polaron stability and delocalization on the magnitude of ferromagnetic coupling is pursued. A lower limit for mild, solution phase $I_2$ doping is established. A comparison of the variable temperature data of various polymers reveals that deleterious antiferromagnetic interactions are relatively insensitive to spin concentration, doping protocols or spin state. Comparison of the various polymers reveals useful design principles and suggests new directions for the development of magnetic organic materials. Novel strategies for solubilizing neutral polymeric materials in polar solvents are investigated.

The incorporation of stable bipyridinium spin-containing units into a polymeric high-spin array is explored. Preliminary results suggest that substituted diquat derivatives may serve as stable spin-containing units for the polaronic ferromagnet and are amenable to electrochemical doping. Synthetic efforts to prepare high-spin polymeric materials using viologens as a spin source have been unsuccessful.

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# Chapter 1. Introduction

**Background**

Magnetism has fascinated humanity since the dawn of time. The Greeks were probably the first to describe the novel properties of lodestone and magnetite, the magnetic iron ore $FeO—Fe_2O_3$. The first magnetic technological invention, the compass, is believed to have originated in China between 2637 B.C. and 1100 A.D. and was known in Western Europe by the twelfth century A.D.[1] A satisfactory explanation of bulk magnetism as a cooperative phenomenon has eluded many of the great scientific minds of the eighteenth and nineteenth centuries and the field was not placed on a firm mathematical foundation until the advent of quantum mechanics and the Pauli exclusion principle early in the twentieth century. An improved understanding of modern experimental and theoretical condensed matter physics has been achieved as a consequence. The experimental observation of new magnetic phenomena, however, continues to challenge the theorist.[2]

Magnetic materials are a ubiquitous feature of the modern world. Common commercial magnets share a number of attributes: they are mostly atom-based, utilize transition or lanthanide-metal-based spin sites, and possess extended network bonding in at least two dimensions. In addition, they are commonly synthesized by high-temperature metallurgical processes. These materials are cheap and effective and are unlikely to be replaced by molecular or polymer-based materials for current applications.[3]

It is anticipated, however, that many systems of the future will be dependent on fast and lightweight magnetic components. Both molecular and organic-based magnets may offer novel properties such as solubility, optical transparency and magneto-optical switching. Their technological application is still in the distant future but these materials are of tremendous intellectual interest.

**Types of Magnetic Behavior**

At least 14 different types of magnetism have been documented to date,[2] but the majority of materials fall into one of five classes of magnetic behavior. These are diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism and ferrimagnetism (Figure 1-1).

Diamagnetism arises from the interaction of electrons paired in a molecular or atomic orbitals and is a property of all matter.

The latter four classes imply the presence of unpaired electrons and are distinguished from each other by their behavior in the presence or absence of a magnetic field. Paramagnetic materials consist of randomly oriented magnetic moments arising from spin angular momenta of unpaired electrons. Magnetic moments order parallel to an applied magnetic field but this configuration can be overcome by thermal energy. There is no net moment in the absence of an applied field.

A ferromagnetic material is characterized by the parallel alignment of electron spins. Bulk ferromagnetism is observed in a solid when all the spins in the material align in the same direction resulting in a macroscopic net magnetic moment. The moment persists in the absence of an applied magnetic field. All ferromagnets become paramagnetic when heated to a sufficiently high temperature. The transition temperature from ferromagnetic to paramagnetic behavior is termed the Curie temperature, $T_c$. Iron, for example has a $T_c = 770°C$.

Antiferromagnetism arises from the anti-parallel alignment of magnetic moments. Many paramagnetic materials align antiferromagnetically at sufficiently low temperatures.

Ferrimagnets represent a final class of magnetic materials. Magnetic moments of unequal magnitude are aligned antiferromagnetically resulting

in a net magnetic moment. Magnetite, $Fe_3O_4$, is perhaps the most familiar ferrimagnet. Like ferromagnets, they may be characterized by spontaneous magnetization below the Curie temperature.

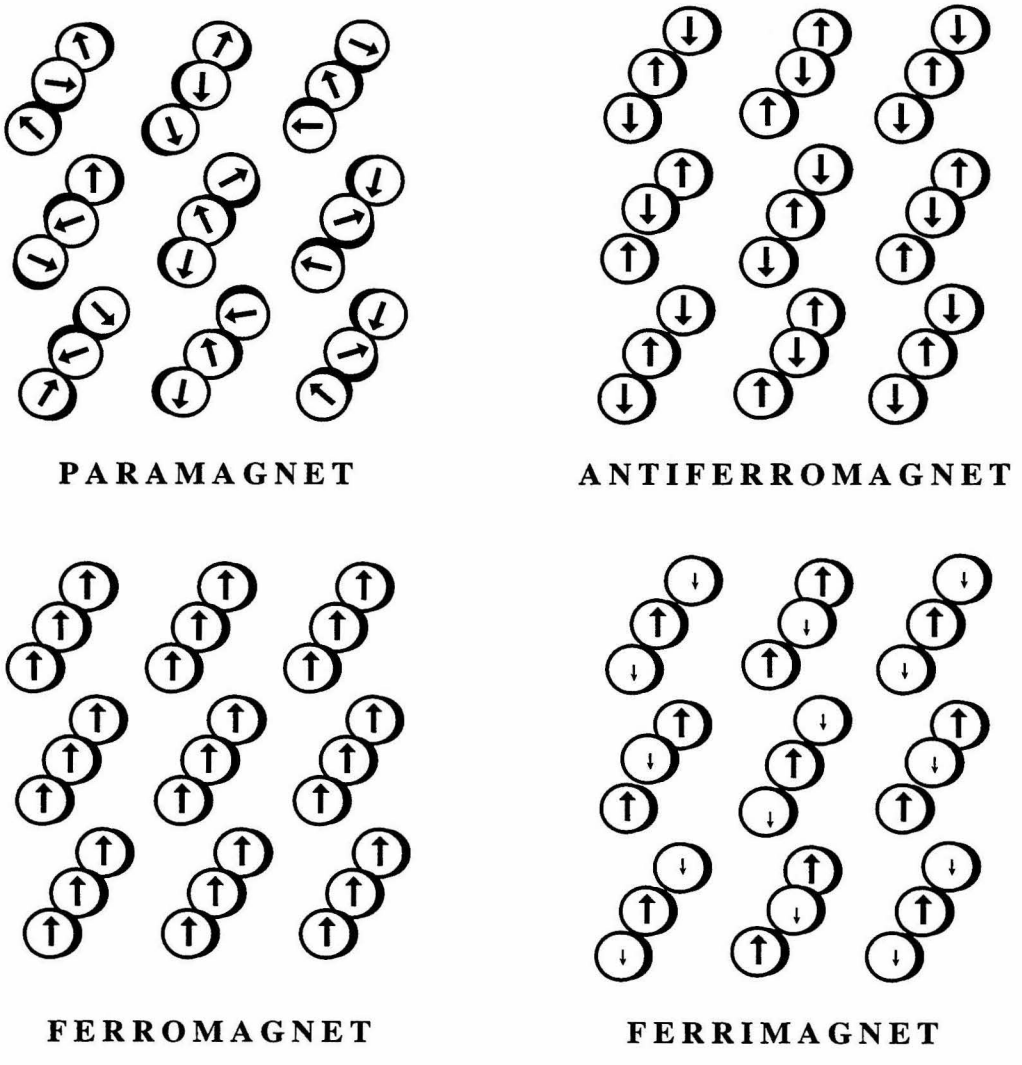
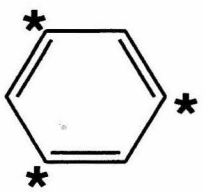
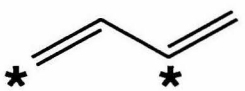


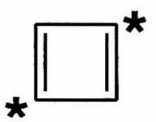

**Figure 1-1.** Four principal classes of magnetic behavior.

**Organic Magnetic Materials**

There are a number of different approaches to the design of molecular ferromagnetic materials. These include McConnell's spin-exchange model,[4 5] and a charge-transfer model developed originally by McConnell[6] and refined by Breslow[7] and Miller.[8,9] A simple topological rule has been developed by Ovchinnikov to predict the ground state of alternant hydrocarbons.[10] The spin state, $S$, of any π-alternant hydrocarbon may be calculated by dividing its atoms into two sets, starred and non-starred, so that no two atoms of the same set are bonded to each other.

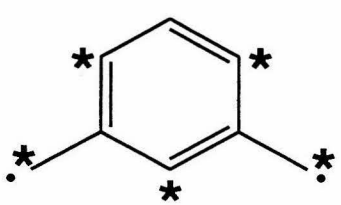




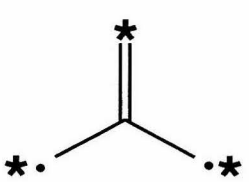


$$S = \frac{n^* - n^0}{2}, \qquad (1)$$

where $n^*$ is the number of starred atoms and $n^0$ is the number of unstarred atoms. Thus, benzene, butadiene and square cyclobutadiene are ground-state singlets, whereas *meta*-quinodimethane, **1**, and trimethylenemethane, **2**, have triplet ground-states.



**1**



**2**

The high-spin preference in these molecules is a consequence of the non-disjoint nature of their NBMOs–they are coextensive in space so exchange repulsions are large (Figure 1-2).[11] The NBMOs of square cyclobutadiene, however, do not span common atoms. Structures such as *meta*-quinodimethane, **1**, are thus considered to be "robust" triplets as the high-spin preference survives changes in geometry and heteroatom substitution.

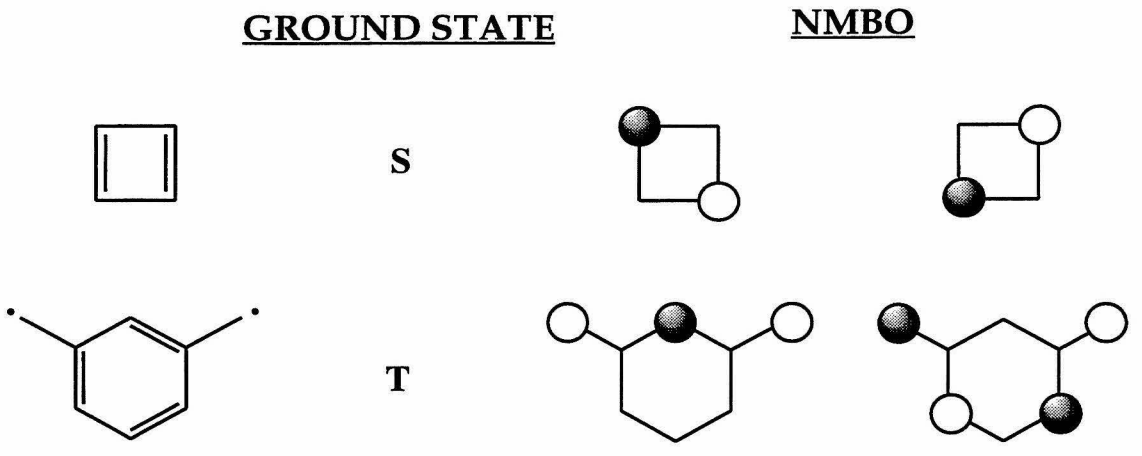
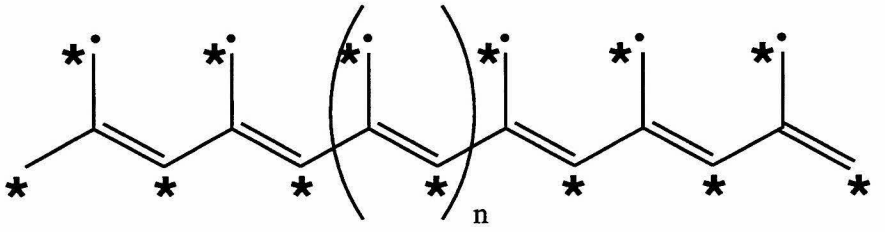



**Figure 1-2.** NBMOs and electronic ground states of square CBD and *m*-xylylene.

An elaboration to polymeric high-spin systems such as **3** can be envisaged where the multiplicity of the material is directly proportional to the number of monomers in the chain.

The polaronic ferromagnet model discussed in this work may be considered to be a perturbation of these systems; delocalized radical cations or anions are high-spin coupled by virtue of their topology. Several examples of ferromagnetically coupled radical cations[12,13] and anions[14,15] have been documented in recent years.



3

**Magnetic Characterization**

The techniques and mathematical formalisms employed to characterize magnetic materials have been reviewed elsewhere[16-18] and are briefly summarized here.

The response of a sample to an externally applied magnetic field, $H$, is termed the magnetic induction, $B$, which includes H and a contribution $4\pi M$ due to the sample itself.

$$B = H + 4\pi M \tag{2}$$

The magnetization, $M$, induced in a material is proportional to the applied field.

$$M = \chi H \tag{3}$$

Experimentally determined magnetic susceptibilities, $\chi_e$, are the sum of diamagnetic susceptibility, $\chi_{dia}$, and paramagnetic susceptibility, $\chi_p$.

$$\chi_e = \chi_p + \chi_{dia} \tag{4}$$

A third term, Pauli susceptibility, $\chi_{Pauli}$, is important in metallic systems but can be ignored for our purposes. The diamagnetic term is small and negative (approximately -1 x $10^{-6}$ emu/mol) and is independent of

temperature. Paramagnetic susceptibility is a positive quantity and is temperature dependent.

**Curie Analysis**

At low fields and high temperature the Curie law is valid and paramagnetic susceptibility is inversely proportional to temperature.

$$\chi_p = \frac{C}{T} \tag{5}$$

$$\chi_e = \frac{C}{T} + \chi_{dia} \tag{6}$$

Thus a plot of observed magnetic susceptibility versus inverse absolute temperature gives a straight line with slope $C$, the Curie constant, and intercept $\chi_{dia}$, upon extrapolation to infinite temperature.

The Curie law may be modified to account for interactions between paramagnetic ions to yield the Curie-Weiss law (7).

$$\chi_p = \frac{C}{T - \theta} \tag{7}$$

This is usually written as:

$$\frac{1}{\chi_p} = \frac{T}{C} - \frac{\theta}{C} \tag{8}$$

The correction term, $\theta$, has units of temperature and is positive for ferromagnetic interactions and negative for antiferromagnetic interactions. A perfect paramagnet has a $\theta$ value equal to zero of course. It is important to note that although $\theta$ detects weak interactions at low temperature, it is determined using *high temperature* susceptibility data where $T \geq 10\theta$.[3,16] Representative Curie-Weiss plots are shown in Figure 1-3.

As very small positive or negative values of $\theta$ are common, it is often

more informative to plot effective moment, $\mu_{eff}$ versus temperature to observe the onset of ferro or antiferromagnetic behavior. Effective moment may be related to molar paramagnetic susceptibility, $\chi_m$, by:

$$\chi_m = \frac{N\mu_{eff}^2}{3\ kT} \tag{9}$$

or

$$\mu_{eff} = 2.824\ \sqrt{\chi_m T} \tag{10}$$

and

$$\mu_{eff} = g\sqrt{S\ (S+1)}\ \mu_B \tag{11}$$

where $S$ is the spin quantum number, $\mu_B$ is the Bohr magneton and $g$ is the Landé constant. Effective moment is then expressed in units of Bohr magnetons.

Thus the spin state of a material of known composition can be determined at any given temperature. In several of our samples, however, the molar susceptibility is not known so we describe our effective moments as "relative" effective moments.

If there are no interactions between neighboring spins, effective moment is constant throughout the temperature range (Figure 1-4). Ferromagnetic interactions between neighboring spins manifest themselves as an upturn in the effective moment plot. A downturn in the effective moment plot is indicative of antiferromagnetic interactions.

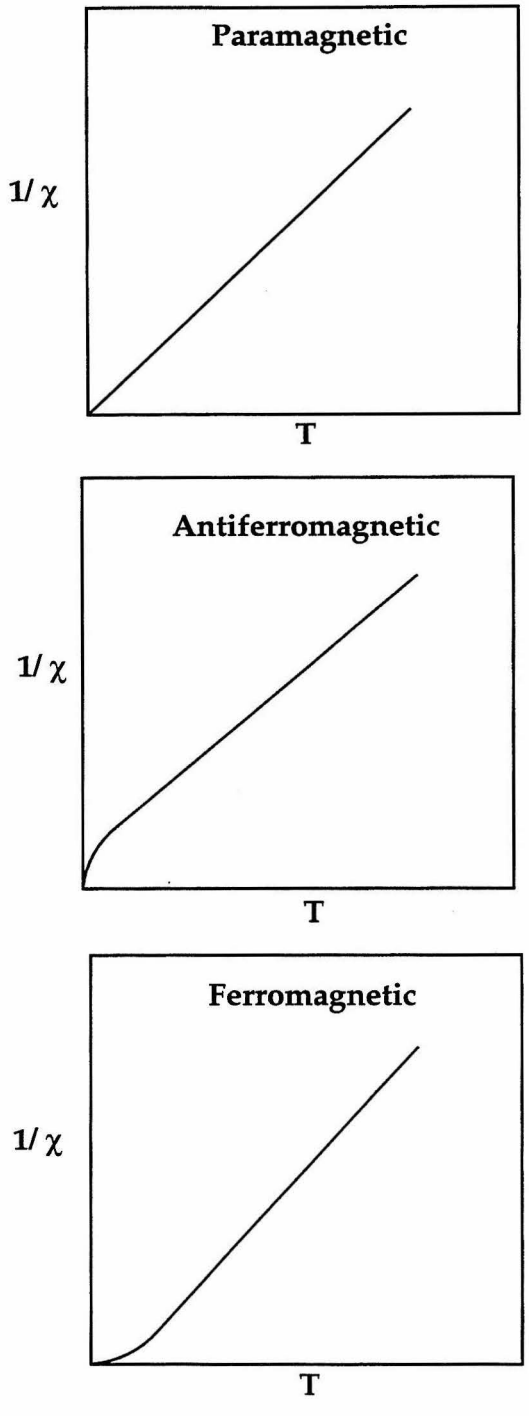



**Figure 1-3.** Idealized Curie-Weiss plots for paramagnetic, antiferromagnetic and ferromagnetic materials.

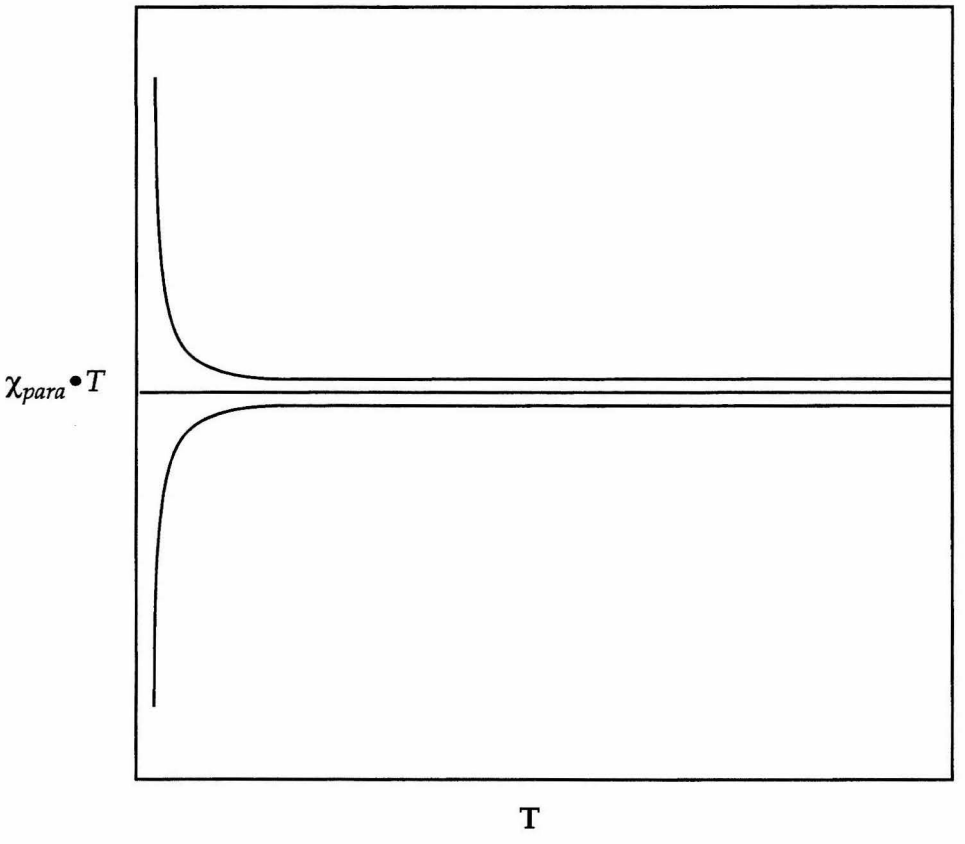



**Figure 1-4**. Idealized relative effective moment plots. The top line, increasing upwards, describes ferromagnetic behavior. The center line is characteristic of an ideal paramagnet whereas the lower line, curving downwards, is indicative of net antiferromagnetic coupling.

**Brillouin Treatment**

The limitations of the Curie law in the determination of spin states of material of uncertain composition have been discussed in the last section. The Brillouin function, $B_S$ , however, allows one to determine the spin state of any given material and is complementary to Curie treatment of magnetic data in some respects.

$$B_S(\eta) = \frac{1}{S}\left[(S+\tfrac{1}{2})\ coth\left[(S+\tfrac{1}{2})\eta\right] - \tfrac{1}{2}coth\ \frac{\eta}{2}\right] \tag{12}$$

where $$\eta = \frac{g\mu_B H}{kT}$$

and

$$M = Ng\mu_B S B_S(\eta) \tag{13}$$

A detailed derivation of the Brillouin function is beyond the scope of this work.[16] It suffices to say that it is valid at low temperatures and high field where $\eta >> 1$. Under these conditions, the function approaches unity; the macroscopic magnetization $M$ becomes saturated and does not change upon further changes in field. All spins are aligned with the field under saturation conditions. Normalized magnetization may be defined as the ratio of magnetization at a given field and temperature, $M_{H,T}$, to the saturation magnetization, $M_{sat}$. This quantity is unitless and is simply the Brillouin function. As a consequence, the spin state of any material may be determined by fitting experimentally determined normalized magnetizations to the Brilllouin function (Figure 1-5). It transpires that for $\eta >> 1$, $H/T >> 0.7$ T/K. Thus for a 5.5 Tesla magnet, a Brillouin treatment of magnetization data is only valid below 6 K.

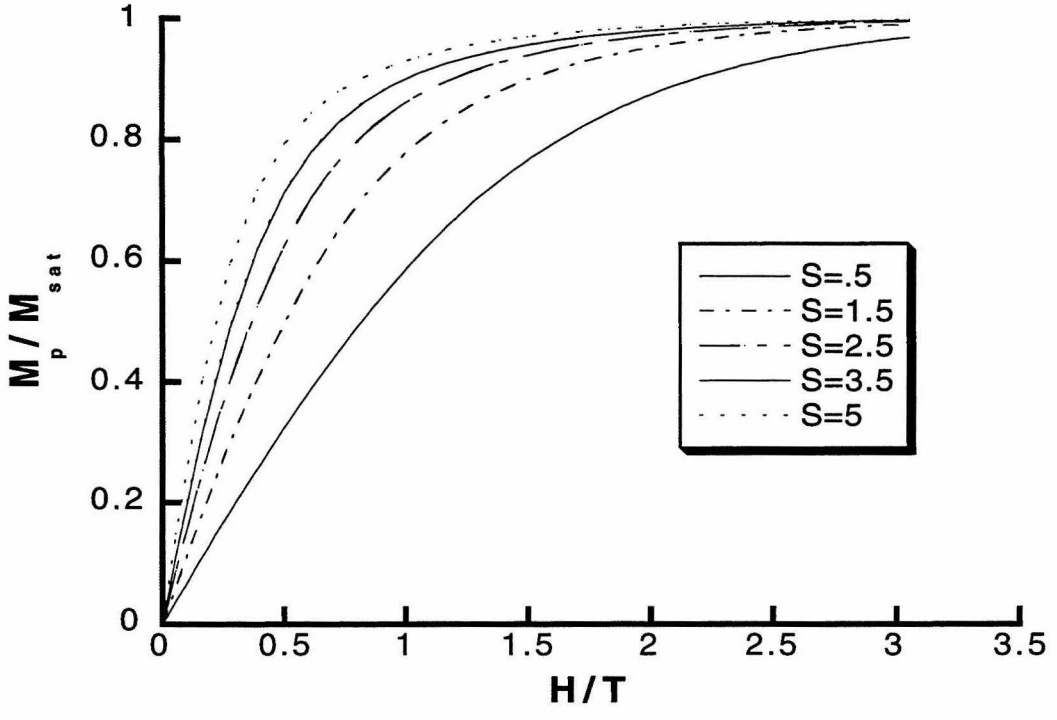



**Figure 1-5.** Theoretical saturation plots for various $S$ values.

Although originally developed for inorganic substances, the Brillouin treatment has also been remarkably successful in determining the spin states of organic materials.[19-22] As the saturation magnetization is directly proportional to the number of spins, Brillouin treatment also allows an accurate determination of spin concentration.

The observed moment, $M_{obs}$, is a composite of paramagnetic moment, $M_{para}$, and a diamagnetic term, $M_{dia}$. One can write:

$$M_{obs} = \chi_{dia}H + M_{sat}B_S(\eta) \tag{14}$$

Fitting programs have been developed that simultaneously evaluate $\chi_{dia}$, $S$ and $M_{sat}$. Alternatively, the diamagnetic correction may be obtained from the variable temperature data and the experimental data subjected to a two-parameter fit.

**References**

(1) Mattis, D. C. *The Theory of Magnetism I;* 2nd ed.; Springer-Verlag: New York, 1988; Vol. 17, pp 295.

(2) Hurd, C. M. *Contemp. Phys.* **1982**, *23*, 469-493.

(3) Miller, J. S.; Epstein, A. J. *Angew. Chem. Int. Ed. Engl.* **1994**, *31*, 385-415.

(4) McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910.

(5) Iwamura, H. *Pure & Appl. Chem.* **1986**, *58*, 187-196.

(6) McConnell, H. M. In *Proc. R.A. Welch Fdn Conf.*; 1967; pp 144.

(7) Breslow, R.; Jaun, B.; Kluttz, R. Q.; Xia, C.-Z. *Tetrahedron* **1982**, *38*, 863-867.

(8) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Science* **1988**, *240*, 40-47.

(9) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Acc. Chem. Res.* **1988**, *21*, 114-120.

(10) Ovchinnikov, A. A. *Theoret. Chim. Acta (Berl.)* **1978**, *47*, 297-304.

(11) Dougherty, D. A.; Grubbs, R. H.; Kaisaki, D. A.; Chang, W.; Jacobs, S. J.; Shultz, D. A.; Anderson, K. K.; Jain, R.; Ho, P. T.; Stewart, E. G. In *Magnetic Molecular Materials*; D. Gatteschi, O. Kahn, J. S. Miller and F. Palacio, Ed.; Kluwer Academic Publishers: The Netherlands, 1991; pp 105-120.

(12) Yoshizawa, K.; Tanaka, K.; Yamabe, T.; Yamauchi, J. *J. Chem. Phys.* **1992**, *96*, 5516-5522.

(13) Yoshizawa, K.; Chano, A.; Ito, A.; Tanaka, K.; Yamabe, T.; Fujita, H.; Yamauchi, J.; Shiro, M. *J. Am. Chem.* **1992**, *114*, 5994-5998.

(14) Tukada, H. *J. Chem. Soc. Chem. Commun.* **1994**, 2293.

(15) Rajca, A.; Rajca, S.; Desai, S. R. *J. Chem. Soc., Chem. Commun.* **1995**, 1957-1958.

(16) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: New York, 1986, pp 1-328.

(17) Kaisaki, D. A. Thesis, California Institute of Technology, Pasadena, California, 1990.

(18) Anderson, K. K. Thesis, California Institute of Technology, Pasadena, California, 1996.

(19) Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *J. Am. Chem. Soc.* **1986**, *108*, 368-371.

(20) Iwamura, H. *Pure & Appl. Chem.* **1987**, *59*, 1595-1604.

(21) Iwamura, H.; Koga, N. *Acc. Chem. Res.* **1993**, *26*, 346-351.

(22) Rajca, A. *Chem. Rev.* **1994**, *94*, 871-893.

# Chapter 2. An Evaluation of Oligothiophenes as Spin Sources for One-Dimensional Polaronic Ferromagnetism

**General Considerations**

Several strategies for developing organic-based ferromagnets have been documented.[1-3] Of these, the polaronic ferromagnet model is perhaps least tested. Early theoretical work by Fukutome[4] suggested that radical cations (polarons) obtained from conjugated organic segments are high-spin coupled when linked through an appropriate π-topology. The structure of a polymeric ferromagnet may be conceptually broken down into two components: spin-containing units (SC) and ferromagnetic coupling units (FC) that ensure high-spin interactions between SCs (Figure 2-1).

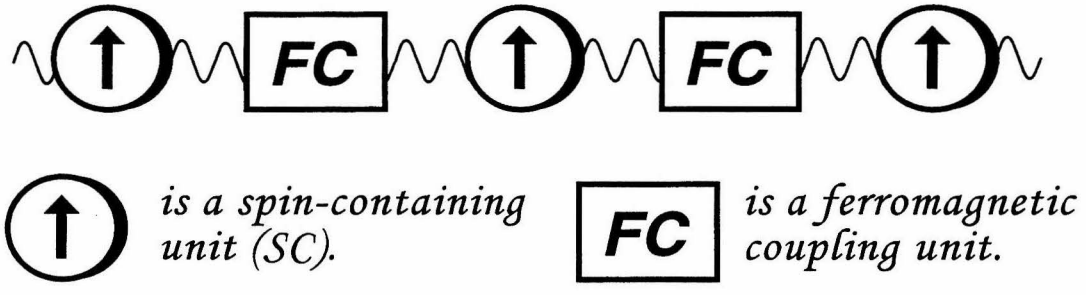



**Figure 2-1**. Schematic design for high-spin polymers. In the polaronic ferromagnet the SC is a polaron.

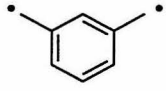
This schematic has proved useful to this group in the design and analysis of high-spin magnetic structures. The defining feature of the polaronic ferromagnet of course is that SC is a polaron. The separation of the polymer into a SC and a FC is somewhat arbitrary, however, as the radical cation (or anion) may delocalize into the FC. It is worth noting that the radical cations described in this dissertation are technically not polarons as they are not part of an infinite, conjugated polymer chain. The ferromagnetic coupling unit disrupts the conjugation by its very nature. Nonetheless, we do feel that

Fukutome's[4] coinage has descriptive value so we have adopted it.

**Design Criteria**

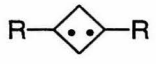
**What Should FC Be?**

The topological requirements for ensuring high-spin coupling in organic systems have been established by studying small molecule biradicals. Three structural motifs are known to enforce cooperative spin behavior. These are *meta*-phenylene[5,6] (shown as *meta*-xylylene), 1,1-ethylene[7] (shown as trimethylenemethane, TMM) and substituted 1,3-cyclobutanediyls (Figure 2-2).[8-10]



*meta*-xylylene

Trimethylenemethane




1,3-Cyclobutanediyl

**Figure 2-2.** High-spin organic topologies.

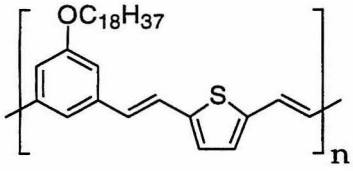
These are considered "robust" ferromagnetic coupling units as a triplet ground state has been demonstrated in several substituted analogs. The singlet-triplet gap is substantial in these systems; triplet states of *meta*-xylylene and TMM are estimated to be 10[11] and 15 kcal/mol[12] below the singlet respectively, whereas the localized biradical 1,3-cyclobutanediyl has a triplet preference of approximately 1.7 kcal/mol.[13] Of these three potential ferromagnetic coupling units, *meta*-xylylene is most readily incorporated into a polymer backbone and is the only FC considered in this work.

**Choice of Spin-containing Unit (SC)**

Although magnetically stable,[14] the biradicals described above are typically

generated by photolysis and are stable only at low temperatures in a solid matrix. Room-temperature stable spins that may be easily generated in high concentration are clearly a better choice for the SC. It is well known from the conducting polymer field that polymers with extended conjugation may be readily oxidized or reduced to produce large numbers of polarons (delocalized radical cations or anions) that may be stable at room temperature.[15,16] Such "doping" may be achieved chemically or electrochemically. This project focuses on the evaluation of a variety of SCs. We evaluate primarily oxidative or *p*-type doping to give radical cations as SCs.

Oligothiophenes were chosen as SCs in this work for the following reasons: it is known from work in the conducting polymer field that polythiophenes often show superior properties to polyacetylene and polypyrrole. Most notably, polythiophene is stable to air and water in its doped and undoped state.[17,18] Polypyrrole is oxidatively unstable in its pristine state whereas polyacetylene is degraded by air and water in both its doped and undoped forms.[15,16] Secondly, sulfur is highly polarizable and thiophene systems are more capable of stabilizing positive charge than their benzene analogs. It has been demonstrated both experimentally and theoretically that thiophene has maximum spin density $\alpha$ to sulfur (see Figure 2-3); these are also the positions most conveniently functionalized. Finally, thiophene's five-membered ring is less susceptible to undesirable steric twisting of the polymer backbone. With these advantages in mind, systems **1-4** were designed and synthesized.

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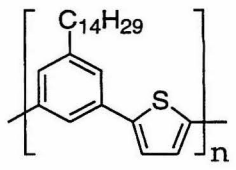


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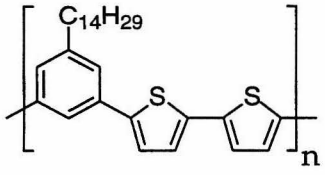


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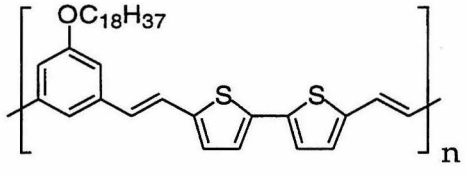


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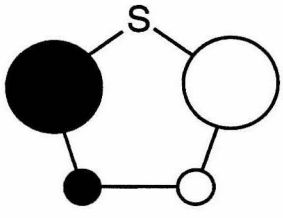
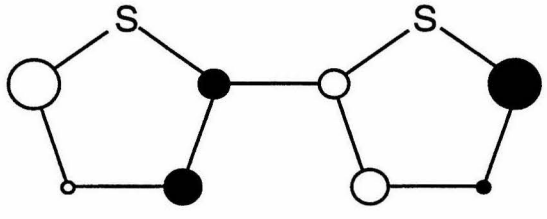



T

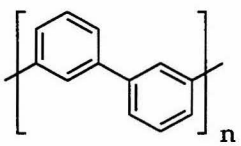



2T

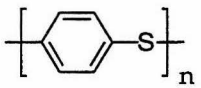
**Figure 2-3.** Hückel highest occupied molecular orbitals of thiophene (T), and bithiophene (2T). Spin density on sulfur is negligible and has been omitted for clarity.[19]

One has to consider whether shorter or longer conjugated segments are better suited to producing a large number of spins which interact strongly through the FC. Ideally one would wish to dope the resulting polymer under the mildest conditions possible, for example $I_2$ rather than more caustic oxidants such as $AsF_5$. The extremely potent oxidizing power of $AsF_5$ is evidenced by high conductivity observed in poly *meta*-phenylene, **5**,[20] and

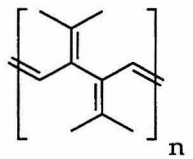
poly *p*-phenylene sulfide, **6**,[21] when extensively doped with this reagent. These systems are nominally insulators as a consequence of interrupted conjugation or poor orbital overlap. Low electrical resistance in these systems is undoubtedly due to extensive cross-linking reactions. Highly twisted Poly (3,4-diisopropylidenecyclobutene), **7**, is believed to be composed of isolated triene units but yields a conductive, paramagnetic material when doped with $I_2$.[22,23] Thus, three double bonds were thought to represent a minimal conjugation length for our purposes.



**5**



**6**



**7**

Since the inception of the conducting polymer field in the 1970s there has been much discussion about the nature of polarons and bipolarons. The length of a polaron, in particular, has been the subject of much speculation. Experimental determination of a polaron's length, however, has only been reported relatively recently. Laser flash photolysis studies suggest polarons are localized to between four and six phenyl rings in poly (*p*-phenylene).[24] The polaronic state of polyacetylene is estimated to comprise units of fifteen independently charged carbon-carbon double bonds.[25] Oligothiophenes (nT) may support two independent polarons if $n \approx 10$, but the bipolaron state is directly produced if $n = 12$.[26]

Two factors favor a short conjugation length. The first of these is the formation of bipolarons. It has been established from the study of conducting polymers that spin-containing polarons may be replaced by *spinless* bipolarons upon prolonged doping (Figure 2-4).[15,16]

# BIPOLARON FORMATION

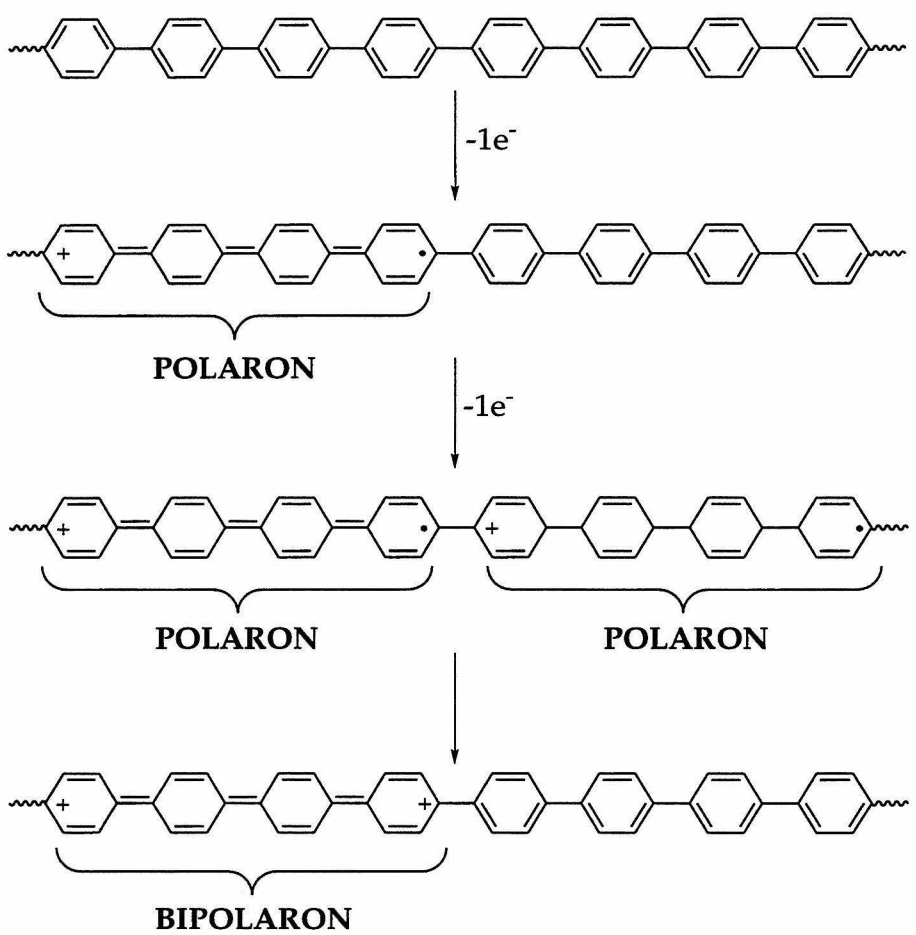



**Figure 2-4.** Polaron formation and annihilation to form bipolarons in poly-*para*-phenylene.

In our design, the spin multiplicity, $S$, of the polymer is proportional to the number of spin-containing units and ferromagnetic coupling units, assuming of course that the system is defect-free. Bipolaron formation is highly detrimental to the polaronic ferromagnet model as bipolarons are diamagnetic and insulate adjacent spins from each other.

It is anticipated that bipolaron formation will be suppressed in shorter SCs due to Coulombic repulsions inherent in a dication (Figure 2-5).

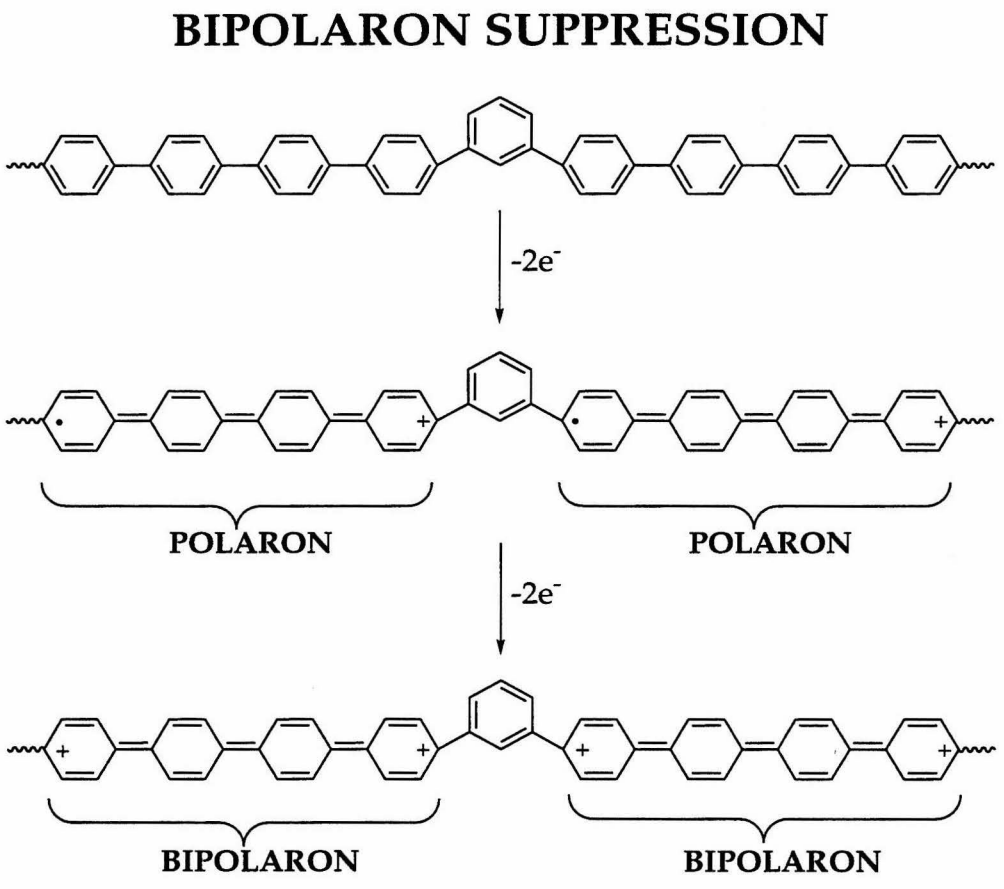
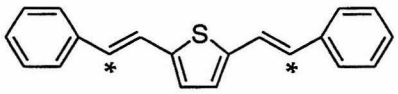



**Figure 2-5.** Bipolaron suppression in *meta*-linked polymeric systems.

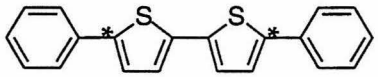
Spin density arguments also favor shorter polarons. It can be reasoned that the effectiveness of the FC scales with spin density at the benzylic positions. There is some experimental evidence for this phenomenon from studies of small molecule tetraradicals in this group.[27] Highly delocalized polarons are predicted to limit the effectiveness of the FC. Spin density is not constant across a polaron but the absolute spin density is certainly less at the

end of a longer polaron. This intuitive reduction in spin density at benzylic positions as the SC becomes more delocalized is apparent at the Hückel level for compounds **8-12** and is depicted in Table 2-1. A diphenyloctatetraene derivative, **12**, is included for comparison. Systems **8-12** serve as models for SCs discussed in this work.

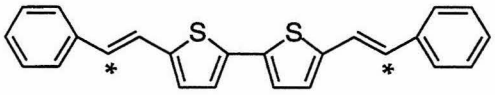


**8**

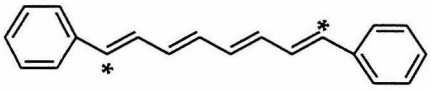
**9**



**10**



**11**



**12**

| Model System | Spin Density (Hückel),% |
|---|---|
| **8** | 14.8 |
| **9** | 18.7 |
| **10** | 14.0 |
| **11** | 11.2 |
| **12** | 14.7 |

**Table 2-1.** Estimated spin densities at benzylic positions for thiophene SCs.

It is gratifying that diminution of spin density at the starred benzylic carbons is relatively gradual. It is conceded that the computational level is

minimal, but extensive EPR measurements on thiophene systems demonstrate a similar trend.[28-30]

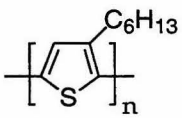
A feature of polaronic ferromagnets that is in stark contrast to conducting polymers is the degree of doping required. Conducting polymers typically show an increase in conductivity of several orders of magnitude when doped. Spin concentration, however, does not usually increase in the same manner. Extensive EPR experiments performed on conducting polymers such as polypyrrole[31] and polythiophene[32] demonstrate an initial rise in polaron concentration upon doping. The paramagnetic signal intensity saturates upon prolonged doping and often diminishes due to bipolaron formation and/or crosslinking of polymer chains. It is expected that a high-spin concentration is required to observe significant cooperative magnetic interactions in the polaronic ferromagnet model.

**Synthetic Concerns**

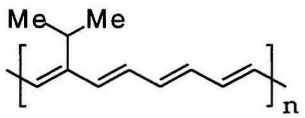
The insolubility of long planar conjugated $\pi$ systems has plagued the conducting polymer field since its inception. Polyacetylene and polythiophene, for example, are both insoluble and infusible. As a consequence, characterization of these systems becomes problematic. There have been several reports in the literature[33] of potentially ferromagnetic polymers that are intractable, insoluble and poorly characterized materials. Germane examples of this behavior include Torrance's iodine complex of poly(1,3,5-triaminobenzene)[34] and Ota's COPNA resins.[35] A common feature of these studies is that there is no distinction between polymerization and introduction of spins. Pristine diamagnetic polymers of known composition are not isolated. These materials may be of potential technological importance but are poor vehicles for detailed structure-activity relationships

and do not permit an understanding of magnetic behavior of organic systems. A detailed characterization of all polymeric materials by common spectroscopic methods such as UV, NMR and IR was considered a priority at the outset of this project. In this way, one could firmly establish that the polymer has the desired topology.

A common method of circumventing the low solubility of conjugated systems is the attachment of long alkyl chains to the polymer backbone. Poly (3-hexyl thiophene), **13**,[36] and Poly (*sec*-butyl cyclooactatetraene), **14**,[37] are freely soluble in common non-polar organic solvents such as benzene, dichloromethane and tetrahydrofuran.




**13**




**14**

It is presumed that crystallization or π–π stacking of alkyl-substituted polymer chains entails a high entropic cost. A similar strategy has been pursued in this work. All polymer systems are designed to be soluble in organic solvents. Highly regioselective polymerization protocols have also been employed to ensure the desired topology is obtained. It is known, for example, that polythiophene obtained by electrochemical or chemical methods has a significant number of undesirable 2-3' linkages.[38] Step-growth (often termed condensation) polymerization protocols are employed exclusively here. Two difunctional monomers are reacted together to generate an alternating block co-polymer as depicted below:

In step-growth systems, the degree of polymerization, *DP*, is dependent on the extent of reaction, $\rho$, as shown:

$$DP = \frac{1}{1-\rho} \tag{1}$$

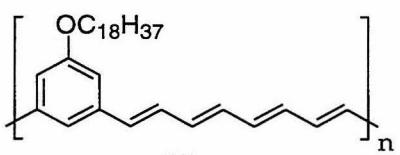
As a consequence, the molecular weights of step-growth polymers only become large if the reaction employed is high-yielding (Figure 2-6). It is extremely important that both reaction partners and solvent are highly pure. The maximum degree of polymerization, $DP_{max}$ , for a stoichiometric ratio r is described by[39]

$$DP_{max} = \frac{1 + r}{1 - r} \tag{2}$$

Traces of monofunctional monomer lead to rapid chain termination and low molecular weight.

**Wittig Polymerizations**

Previous work in this group[40] and others[41-44] has demonstrated that Wittig condensations of phosphonium bisylides with bisaldehydes yield polymers of acceptable molecular weights (Scheme 2-1). An early prototype of a polaronic ferromagnet, Poly (*meta*-phenyleneoctatetraene), abbreviated to PMPOT, **15**, was synthesized in this fashion and yielded a soluble polymer with a degree of polymerization of approximately 22.[40]




**15**

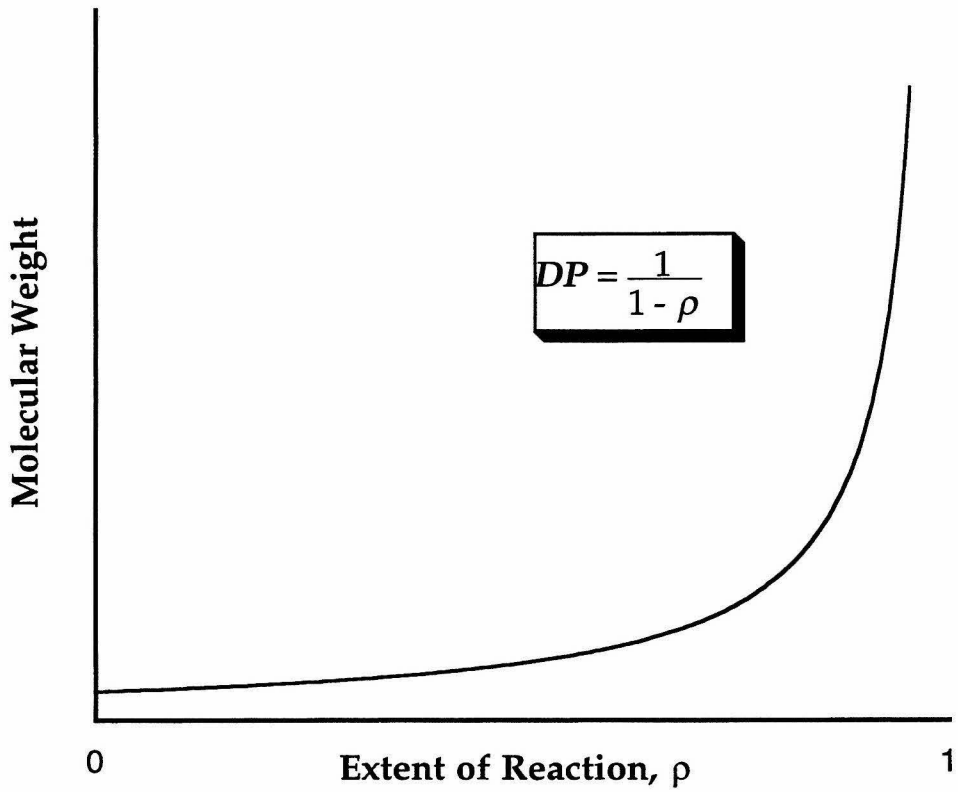
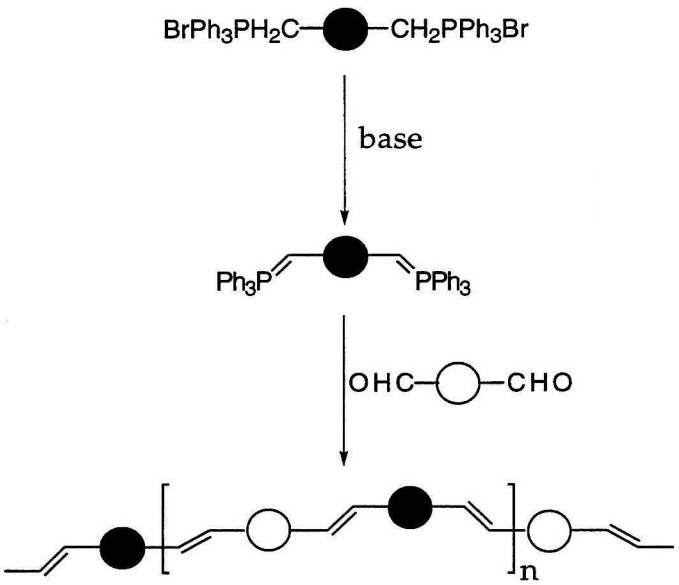



**Figure 2-6.** Plot of molecular weight versus extent of reaction for step-growth polymerizations.

**Scheme 2-1**



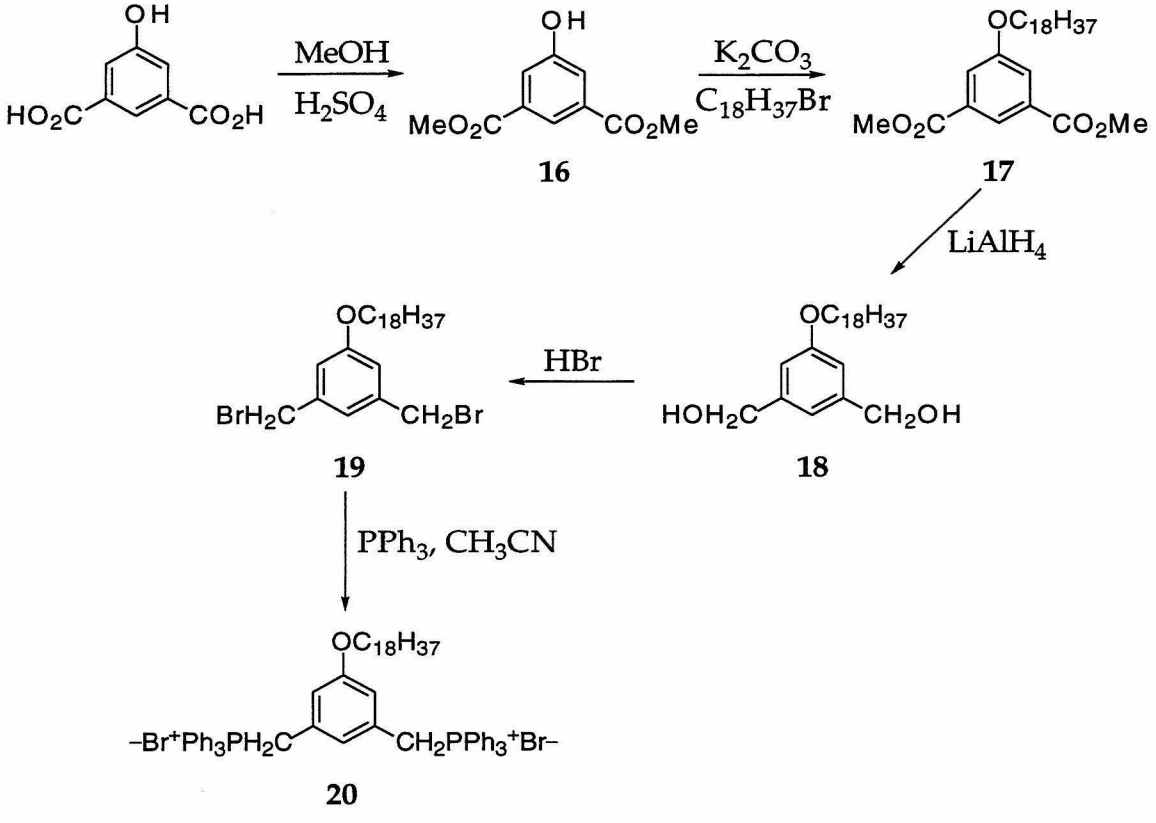

An adaptation of this synthetic method was used in early studies and proved to be moderately successful in attaining high molecular weights of soluble polymer. Initial systems synthesized are **1** and **4**. These are referred to as derivatives of poly *meta*-phenylene, (PMP). Other building blocks are 2,5 thiophene (**T**) and vinylene (**V**). Thus **1** may be named poly *meta*-phenylene vinylene thienylene vinylene or PMPVTV and **4** is analogously named PMPVTTV.

A subtle steroechemical point concerning Scheme 2-1 should be made here. Carbon-carbon double bonds are depicted in an all *E* arrangement. In reality, reaction conditions are more likely to favor *Z* isomers.[45] It has been demonstrated in all-*Z* polyacetylene derivatives, however, that reversible electrochemical doping converts the polymer irreversibly to the all-*E* isomer.[37] Catalytic amounts of iodine in the presence of light achieve the same objective.[46] It is unlikely, therefore, that this stereochemical

uncertainty will be an issue in doped systems.

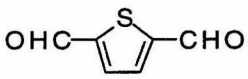
An improved synthesis of the bisphosphonium salt has been developed from commercially available 5-hydroxyisophthalic acid and is outlined in Scheme 2-2.

**Scheme 2-2**

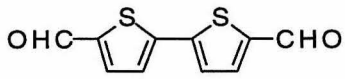



Earlier approaches used a mixture of carbon tetrabromide and triphenylphosphine to brominate diol **18** in low yield. It has been found that gaseous HBr in dry benzene affords dibromide **19** virtually quantitatively. In addition, acetonitrile has proved to be a more practical solvent than DMF in the synthesis of bisphosphonium salt **20**. Bisphosphonium salt **20** may be condensed with the appropriate bisaldehydes **21** and **22** to yield desired

polymers **1** and **4** (Scheme 2-3).

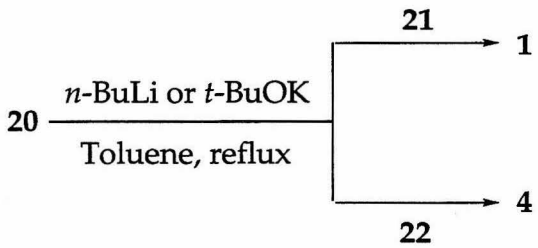


**21**



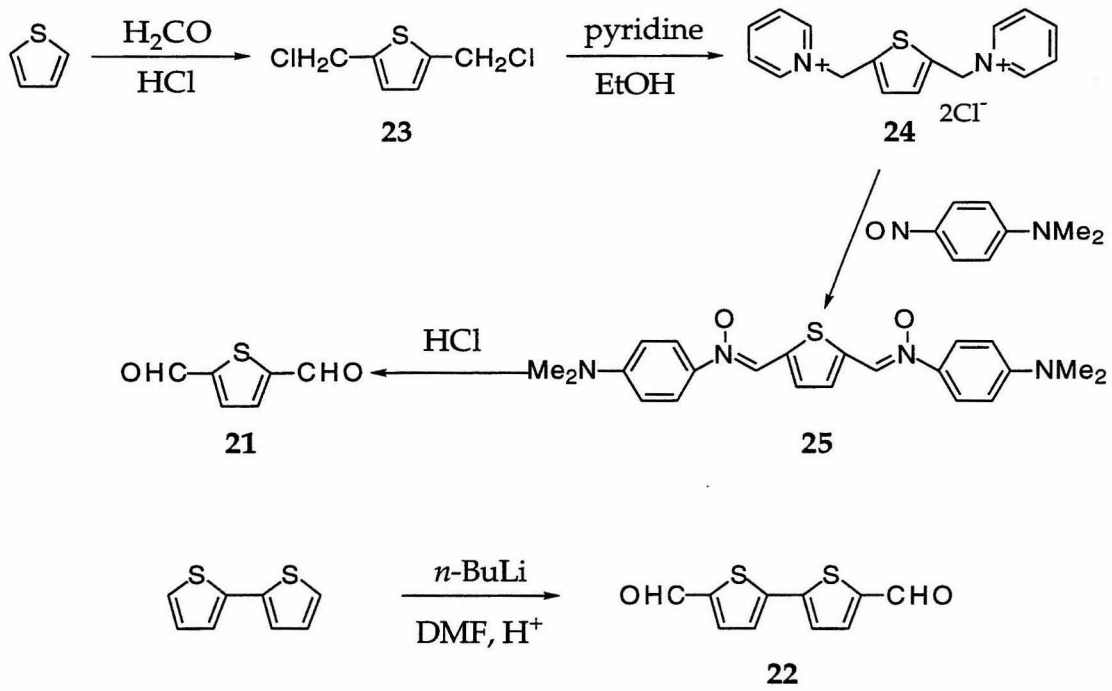
**22**

**Scheme 2-3**




The monomers themselves are known compounds and their syntheses are outlined in Scheme 2-4. 2,5-Thiophenedicarbaldehyde was synthesized in a four step sequence starting from thiophene itself.[47] Briefly, thiophene is chloromethylated by formaldehyde and hydrochloric acid. Treatment with pyridine in absolute ethanol yields the highly hygroscopic bispyridinium salt, **24**. Reaction with 4-Nitroso-*N*,*N*-Dimethyl aniline affords bisnitrone **25** in moderate yield. Subsequent hydrolysis in concentrated hydrochloric acid yields the desired bisaldehyde. A more efficient one-pot bismetallation procedure has since been developed.[48] 2,2'-Bithiophene-5,5'-dicarbaldehyde **22** was obtained by dimetallation and subsequent formylation of commercially available 2,2'-Bithiophene.[49]

**Scheme 2-4**




Early protocols necessitated careful titration of *n*-butyl lithium before generation of the bisylide. It was found that potassium *tert*-butoxide serves equally well as a base and may be added in excess with virtual impunity, thus simplifying the procedure.

The Wittig reaction, however, is generally not considered to be a good polymerization method; yields are often as low as 70% and high polydispersity indices are common. Separation of the side product, triphenylphosphine oxide, can be time-consuming. Furthermore, isolated carbon-carbon double bonds are a potential reactive site. Simple Hückel calculations demonstrate that there is a minimal reduction in spin density at the key benzylic position upon substituting two carbon-carbon double bonds with a five-membered aromatic ring. Other polymerization strategies that

allow direct coupling of aryl rings were investigated as a consequence.

**Palladium-Mediated Polymerizations**

Group VIII transition metals, particularly nickel and palladium, are effective in catalyzing the cross-coupling of organometallic species with organic halides according to Figure 2-7.[50] Several organometallic reagents have proved to be useful as the nucleophilic component in the cross-coupling reaction and all follow the mechanistic pathway depicted in Figure 2-7. Less electropositive metals such as Sn, Zn and B have demonstrated better functional group compatibility than earlier work with Grignard reagents.[51] Stille has demonstrated the utility of organotins in this context.[52,53] Transfer of organozinc reagents to aromatic halides has been extensively investigated by Negishi.[54] More recently, Suzuki has demonstrated that arylboronic acids undergo facile cross-coupling with aromatic bromides or iodides in the presence of aqueous base and a palladium(0) catalyst.[55] The reaction is high-yielding, and has excellent functional group tolerance. Organoboronic acids are generally thermally stable to both air and oxygen and generate non-toxic side-products which can be easily removed. Moreover, the protocol has been used with great success in the synthesis of soluble high molecular weight poly *para*-phenylenes,[56] **26**, water-soluble poly (*para*-phenylene),[57] , **27**, fused polycyclic polyphenylenes,[58] , **28**, and dendrimers,[59] **29** (Figure 2-8).

Oxidative addition of the halide to the metal center is often the rate-determining step in these Pd(0) catalytic cycles. As a consequence, electron deficient aromatic halides are highly reactive partners in this reaction class. We are limited in this regard as far as thiophene is concerned because thiopheneboronic acids are known to deboronify upon prolonged heating in aqueous base. Thus, a *meta*-bisboronic moiety with a solubilizing group in

the 5 position was designed and synthesized. Catechol esters are superior to free boronic acids as they are usually highly crystalline materials and are easily purified. The efficient synthesis of the key building block **33** is outlined in Scheme 2-5.

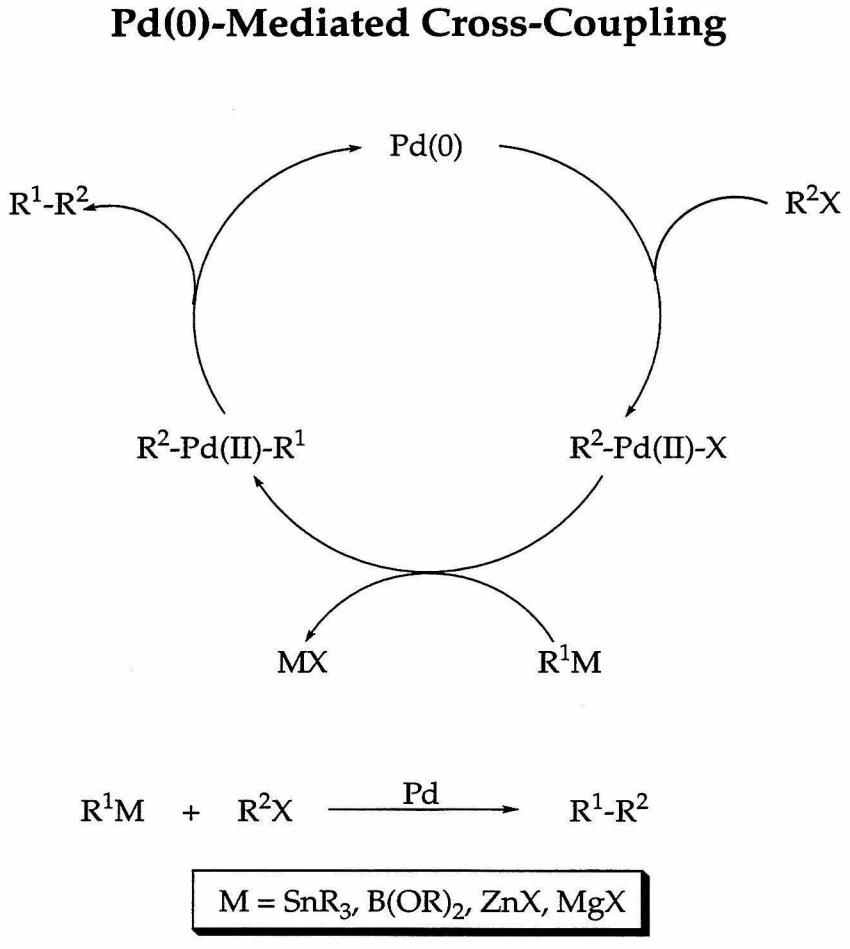



**Figure 2-7.** A general catalytic cycle for cross-coupling.

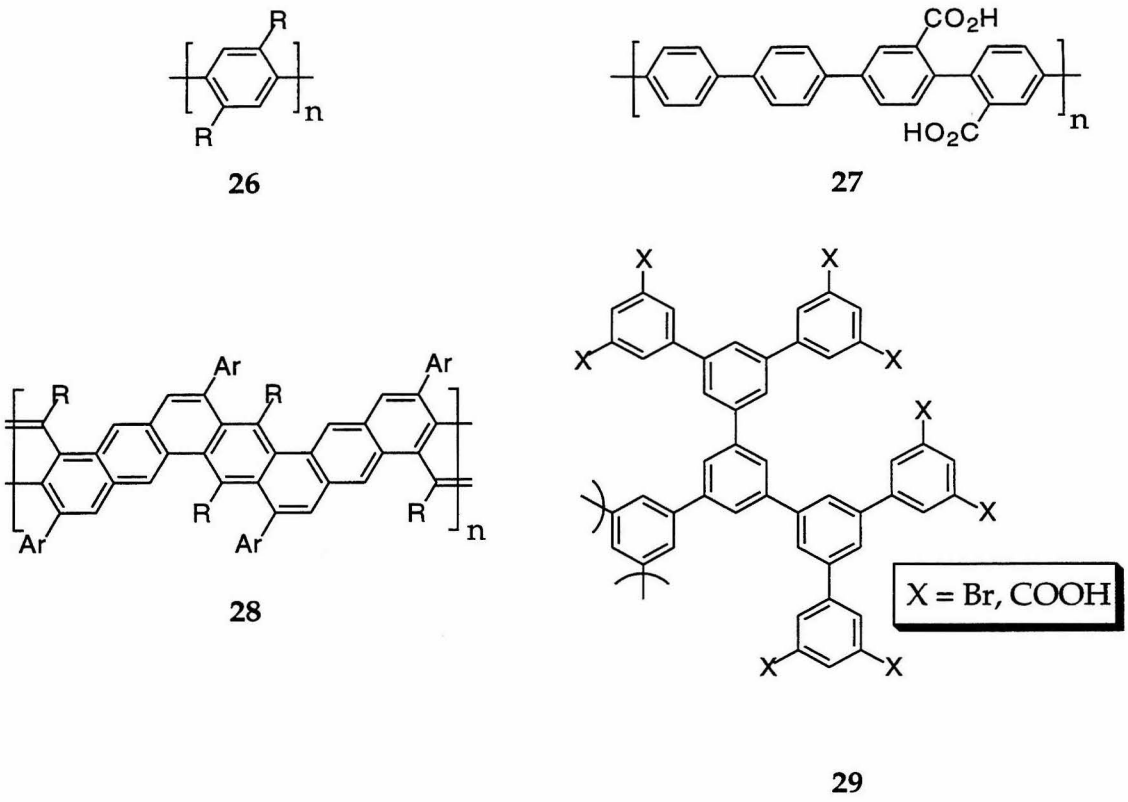
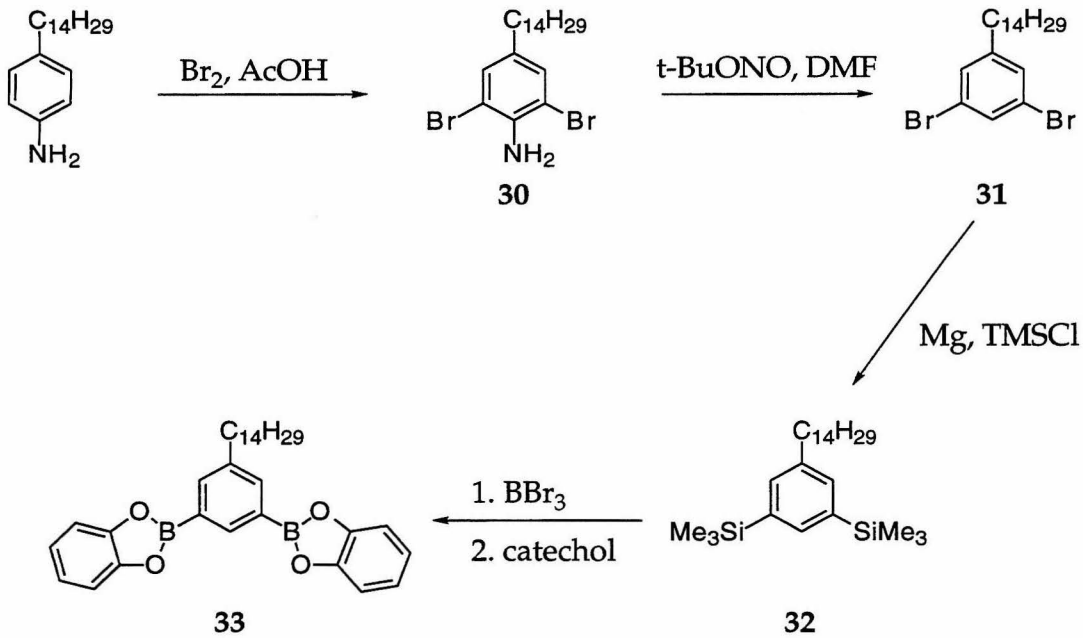


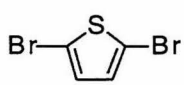

**Figure 2-8.** Aromatic rigid-rod polymers synthesized via Suzuki coupling.

Commercially available 4-tetradecylaniline provides convenient access to a solubilizing chain and a directing group to furnish the desired *meta* topology.[60] Bromination in glacial acetic acid yields **30** in greater than 90% yield. Reductive deamination with tert-butyl nitrite[61] in DMF affords dibromide **31**. Subsequent generation of the bis Grignard compound and reaction with trimethylsilyl chloride yielded crude **32**. No appreciable reaction was detected upon reaction of **32** with bromocatechol[62] but treatment with boron tribromide[63] and catechol[64] furnishes **33** as an easily purified solid.

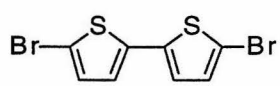
**Scheme 2-5**




Dibromothiophenes **34** and **35** are readily available and the synthesis of the corresponding polymers **PMPT**, **2**, and **PMPTT**, **3**, is outlined in Scheme 2-6.

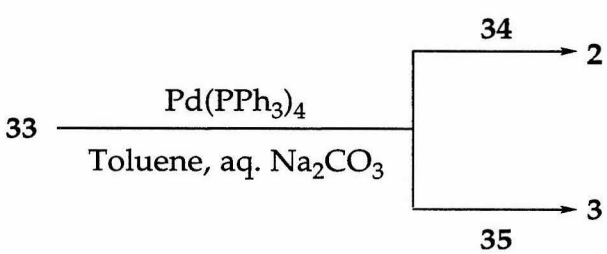



**34**




**35**

**Scheme 2-6**



**Polymer Characterization**

Systems **1, 2, 3** and **4** were all sufficiently soluble to allow complete characterization by conventional methods. Gel permeation chromatography, (GPC), versus a polystyrene standard indicated that number average MW ≈ $10^4$ in each case indicative of 10-30 monomer units on average per polymer chain. Polymer **3**, however, was only sparingly soluble in methylene chloride and its molecular weight as determined by GPC is probably a lower limit. In addition, unlike the other polymers, **3** could not be cast as a thin film on a teflon block or glass slide. It is encouraging to note that Suzuki polymerizations yield polymers of lower polydispersity index than their Wittig counterparts. The relatively high molecular weight of all these systems is confirmed by the absence of endgroups as determined by elemental analysis.

$^1$H NMR spectra are broad due to slow tumbling of polymer chains as typically observed in solutions of organic polymers. The absence of significant aldehyde, phosphonium or boronic acid endgroups is determined. In addition, the lack of contamination by triphenylphosphine oxide, catechol or other side products may be confirmed.

IR spectroscopy is relatively uninformative for analysis of polymers synthesized by palladium-mediated catalysis but is somewhat useful in confirming high molecular weight in Wittig polymerizations. Absorptions characteristic of aldehydes in the 1650-1800 $cm^{-1}$ region are weak or non-existent.

The interrupted nature of conjugation in these systems is emphasized by comparing the optical absorption spectra of **1, 2, 3** and **4**. In contrast to conducting polymers, the absorption maximum is not a function of polymer chain length. Rather, values of $\lambda_{max}$ are solely dependent on the conjugation

length of the SC (Table 2-2). If the SCs may be considered as isolated units, then the bathochromic shift reflects a narrowing of their HOMO-LUMO gap.

| Polymer | $\lambda_{max}$ | Observed Color |
|---|---|---|
| **1** | 410 | yellow |
| **2** | 345 | pale yellow |
| **3** | 390 | yellow |
| **4** | 432 | orange |

**Table 2-2.** Optical absorption maxima of thiophene polymers.

**Doping Protocols**

Two different doping protocols were pursued in these early studies namely exposure to gaseous $AsF_5$ and solution phase doping with iodine. Early work in this group[65] established that gas phase and solution phase iodine doping produced similar results. The latter approach is far more convenient and is emphasized in this work. Gas phase $AsF_5$ doping was performed on thin (40-60 μm) films cast from chloroform solution onto teflon block or a glass slide. Because of its insoluble nature, **3** was doped as a loose powder. Two distinct $AsF_5$ doping regimes are described here. "Light" doping refers to exposure to 50 Torr of $AsF_5$ for 30 minutes whereas "heavy' doping indicates exposure to 200-300 Torr for 5-7 hours. The heavy doping conditions were modified somewhat from earlier studies as it was found that there was no substantial increase in spin concentration upon exposure of thin films to 400 Torr for 24 hours.

**Instrumentation Concerns and Magnetization Studies**

EPR has been an invaluable tool in the determination of high-spin ground

states since its invention in the 1940's. The technique is highly sensitive and can readily detect very small concentrations of paramagnetic species. Moreover, variable temperature studies allow an estimation of the energy gap between various spin states. It has been applied with great effectiveness to small organic and inorganic molecules, but is of limited use in polymeric systems such as those discussed here.[66] EPR fine structures are averaged out due to exchange narrowing for neat radicals and thus high-spin molecules must be diluted in a solid solution matrix or in mixed crystals. In addition, the principal axis of the zero-field tensor must be aligned with the magnetic field to facilitate a rigorous analysis of the zero-field splitting parameters. Otherwise, complex powder patterns are the consequence. Finally, it is difficult to measure long-range spin ordering and distinguish between ferro or antiferromagnetic couplings. Polymeric materials are typically disordered and it is expected that polaronic systems will have several chemically non-equivalent magnetic centers and an array of possible magnetic transitions. It is expected, therefore, that EPR signals will be broadened considerably.

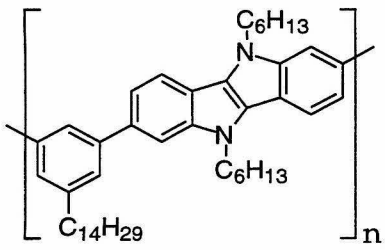
Magnetometry, or the measurement of magnetic susceptibility, may be considered as a complementary technique for small molecules but is especially useful for polyradical systems. We employ a Quantum Design Magnetic Property Measurement System (MPMS) for our measurements. A ±5.5 Tesla variable field magnet surrounds a gradient, second derivative array superconducting quantum interference device (SQUID) magnetometer designed to reject the field due to the superconducting magnet. The device is based on a Josephson junction, which is very sensitive to changes in magnetic flux and allows the measurement of very small magnetic moments ($10^{-12}$ emu/gram).[67] This technique allows the determination of the spin state of weakly magnetic materials and is quite amenable to polymer samples. The

temperature of the sample region may be varied between 1.7 and 400 K allowing variable temperature studies.

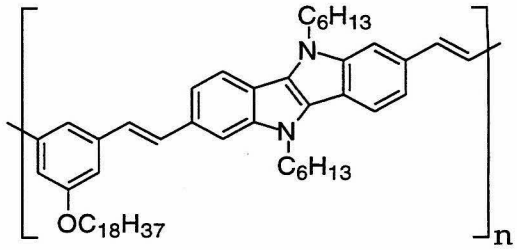
A major obstacle in these measurements is the difficulty in providing a small, homogeneous background signal. Paramagnetic susceptibilities are usually three to six orders of magnitude larger than diamagnetic susceptibilities but the diamagnetic correction may become quite substantial for weakly paramagnetic samples such as those discussed here. As the field-dependent paramagnetic susceptibilities are positive whereas field-independent diamagnetic susceptibilities are negative, it is conceivable that the total magnetic susceptibility changes sign upon moving from low to high field. This was observed in early sample geometries employing a paramagnetic polymer embedded in a gelatin capsule with glass wool. Paramagnetic and diamagnetic contributions to the observed moment were often not spatially coincident when the moment passed through zero and the moment reported by the SQUID was inaccurate. A magnetically homogeneous delrin holder was designed to ensure that the total moment was greater than zero at all field strengths, simplifying the analysis considerably.[68]

**Magnetic Characterization of Doped Polymers**[69]

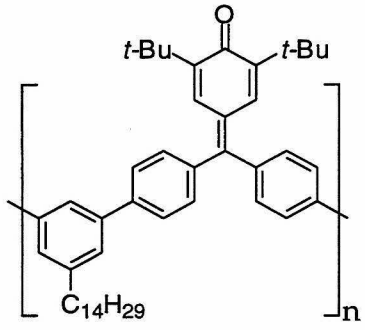
This section describes the magnetization behavior of thiophene polymers PMPVTV, PMPT, PMPVTTV, and PMPTT. Data analysis methods are described in some detail for PMPVTV; other polymer systems were treated in a similar manner. Results are compared to previously studied PMPOT and three other prototypes for the polaronic ferromagnet studied in this group namely PMPII, PMPVIIV and PMPF.




**PMPII**




**PMPVIIV**




**PMPF**

**Background**

It has already been discussed that these one-dimensional systems are not expected to spontaneously order into a ferromagnet. There is no control over magnetic interactions in the second and third dimensions; it is expected that these will be *antiferromagnetic* in nature as is usually the case. These studies are designed to probe *intramolecular* spin-spin interactions and to determine whether or not these spin centers are simply isolated polarons with an $S$ value of $^1/_2$ or if there is some local high-spin coupling between polarons as demonstrated by $S$ values $> {}^1/_2$. The spin state *(S)* of any paramagnetic material may be obtained from a plot of magnetization *(M)* versus applied field *(H)* at constant temperature *(T)*. As the field increases, the induced moment increases until all the spins are aligned with the field. There is then no further increase in $M$ when the field is increased. This is termed the

*saturation* condition and the $S$ value of a material may be determined by examining the rate at which it saturates. This may be quantitatively modeled by the Brillouin function.[70] This group has developed fitting procedures that allow an evaluation of $S$ value by fitting the function to experimental data.

The extent of doping may also be determined from variable field measurements. The saturation magnetization $(M_{sat})$ may be converted to absolute spin concentration and these are reported as the percent of monomers doped. Technically, we refer to the percent of monomers that contain a spin.

**The Meaning of *S***

The S value derived from the Brillouin fitting procedure is certainly an average from a complex mixture of sites.[71] For example $S = 2.0$ suggests that four polarons are ferromagnetically coupled to each other, but it does not mean that every spin is part of a four-spin cluster. If this were so, the saturation data would fit exactly to the Brillouin function. This is never the case. Rather, the observed $S$ value represents an approximation to a mixture of different spin states. Recall that magnetization, $M$, is related to the product $SB_S$ where the Brillouin function $B_S$ corresponds to spin $S$ by a spin-independent factor, $Ng\mu_B$.

$$B_S(\eta) = \frac{1}{S}\left[(S+\tfrac{1}{2})\ coth\left[(S+\tfrac{1}{2})\eta\right] - \tfrac{1}{2} coth\ \frac{\eta}{2}\right] \tag{3}$$

where $$\eta = \frac{g\mu_B H}{kT}$$

$$M = Ng\mu_B S B_S(\eta) \tag{4}$$

The addition of magnetizations for two different spin states $S_1$ and $S_2$

would imply the addition of $Ng\mu_B S_1 B_{S1}$ and $Ng\mu_B S_2 B_{S2}$. This does not give a product of spin and Brillouin functions $Ng\mu_B S B_S$. At low values of $H/T$, $M \propto S(S + 1)$ whereas $M \propto S$ at large values of $H/T$. Thus, the saturation plot is dominated by large $S$ values at low values of $H/T$ and by low $S$ values at higher values of $H/T$. One would expect that the data lies above the curve fit at low field and below the curve at high field. Such behavior is generally observed in our fits and is illustrated in Figures 2-11 for an equimolar mixture of $S = 2.5$ and $S = 0.5$ species. The deviation of best fit $S$ from the arithmetic mean can be quite significant if the two spin states differ greatly in magnitude. For comparison, the fitted $S$ values for varying compositions of triplet and quintet species are within 10% of their arithmetic mean.[68]

**Estimation of the Diamagnetic Correction**

An estimation of the diamagnetic correction of organic molecules is often determined by referencing Pascal's constants. Such an analysis is not amenable to samples of unknown composition and the values often vary from compound to compound.[70] A more reliable estimate may be made from either variable field or variable temperature magnetization studies. A three parameter fit to variable field data at constant temperature allows a simultaneous evaluation of $M_{sat}$, $S$ and $\chi_{dia}$. Alternatively, a plot of $\chi_e$ versus inverse absolute temperature yields a straight line in a temperature regime where the Curie law is valid. The diamagnetic correction can then be estimated by extrapolation to infinite temperature. This author has found that the latter approach is superior in a number of different scenarios. The three parameter fit inevitably overestimates the correction (and, as a consequence, *overestimates* $S$ and *underestimates* spin concentration) when the moment is very large; this temperature independent term is often larger

than the correction observed for the empty delrin holder itself which is preposterous for the following reason. The susceptibility, (typically 3-8 x $10^{-8}$ emu•G), of the empty holder is positive as it actually is a measurement of the *absence* of a diamagnetic sample. Adding any material to the sample space is thus expected to *reduce* the observed diamagnetic term. This behavior is independent of $S$ value and has been observed for transition metal complexes with high-spin states and strong paramagnetic responses. The correction should be negligible in these cases of course. This fitting procedure is also inferior when considering samples with $S$ values very close to $^1/_2$ as the Brillouin function is not close to saturation at these $S$ values. The diamagnetic correction derived from variable temperature data, however, is in a reasonable range. Variable temperature data obey Curie's law typically in the range 50-200 K. For these reasons all susceptibility data reported here use a correction from variable temperature plots at constant field.

**PMPVTV, 1**

This system is closely related to PMPOT, **15**, a system studied earlier in this group.[65] The magnetization behavior of PMPOT is reviewed briefly here. It was demonstrated that four polarons ferromagnetically couple on average when PMPOT is doped with low pressures of $AsF_5$. A light doping protocol was developed previously in this group for this material. The variation in $M_{sat}$, an indication of the total number of spins, with length of exposure is outlined in Figure 2-10. There is a rise, followed by a small turnover at longer exposures. There is some variability of course from run to run in these studies but the basic pattern of Figure 2-10 is seen and establishes a basis for the light doping protocol.

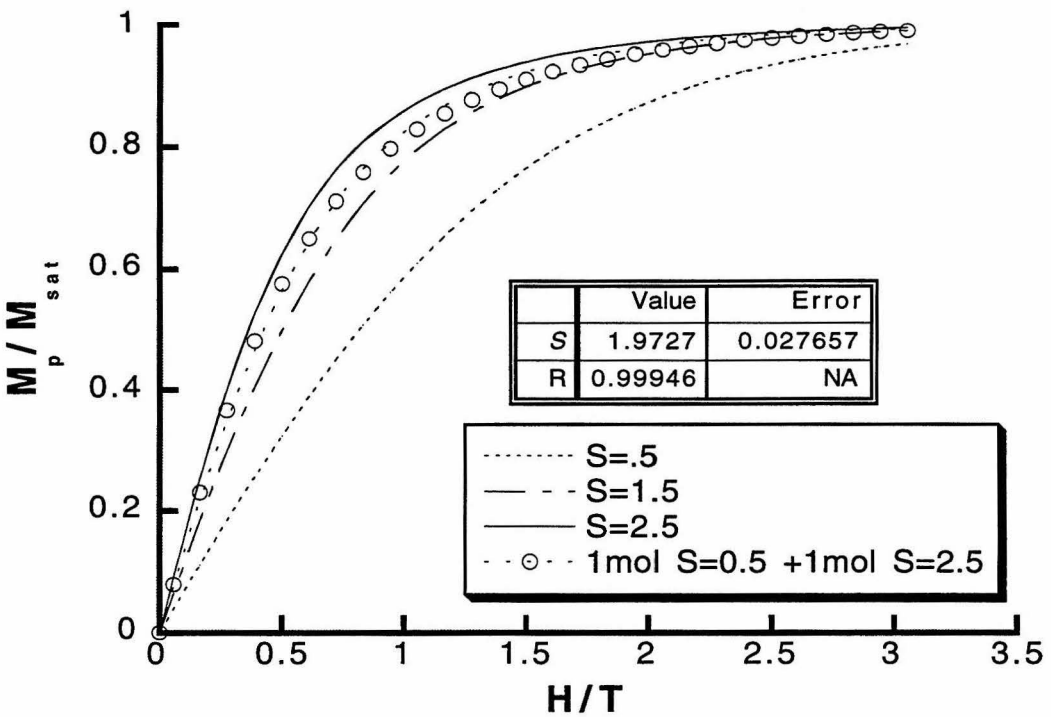
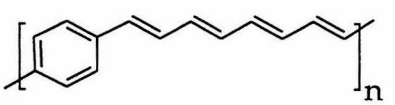



**Figure 2-9.** A Brillouin fit to an equimolar mixture of $S$ = 2.5 and $S$ = 0.5. Note that the fitted S value differs substantially from the arithmetic mean $S$ = 1.5 and that there is a crossover from the larger $S$ function to the lower $S$ function with increasing $H/T$.

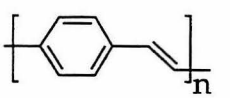
Prolonged doping of PMPOT with $AsF_5$ yielded a highly paramagnetic material which can be fit to $S = 0.5$. In heavily doped polymer samples dopant uptake by mass is considerably larger than that suggested by $M_{sat}$. This could be a consequence of bipolaron formation, cross-linking, or dopant "clustering" (e.g., to form $As_2F_{11}^-$ or $As_3F_{16}^-$). Antiferromagnetic interactions between polarons is another factor that could diminish measured spin concentrations. These interactions are problematic as $M_{sat}$ is determined at low temperature (usually 1.8 K).

The nature of the counterion in $AsF_5$-doped samples of polyacetylene and polyparaphenylene is the subject of some controversy but it has been established that it is *not* paramagnetic $AsF_5^{\bullet -}$.[72] Hence, spins generated upon oxidation of these polymers by $AsF_5$ are located on the polymer backbone.

Milder solution phase and gaseous phase iodine doping gave slightly lower $S$ values ($S \approx 1$-1.5) than light $AsF_5$ doping . Control polymers PPPOT and PPPV did not exhibit any high-spin coupling between polarons when doped under the same conditions. Hence, the observed cooperative spin communication is a consequence of the material's *meta*-linked topology.



**PPPOT**



**PPPV**

The structural perturbation from PMPOT to PMPVTV is minor, four double bonds of the SC have been replaced by a thiophene and two double bonds. Nonetheless, it was hoped that spins produced upon doping would be more stable. As it transpires PMPVTV behaves very similarly to PMPOT in terms of its doping behavior.

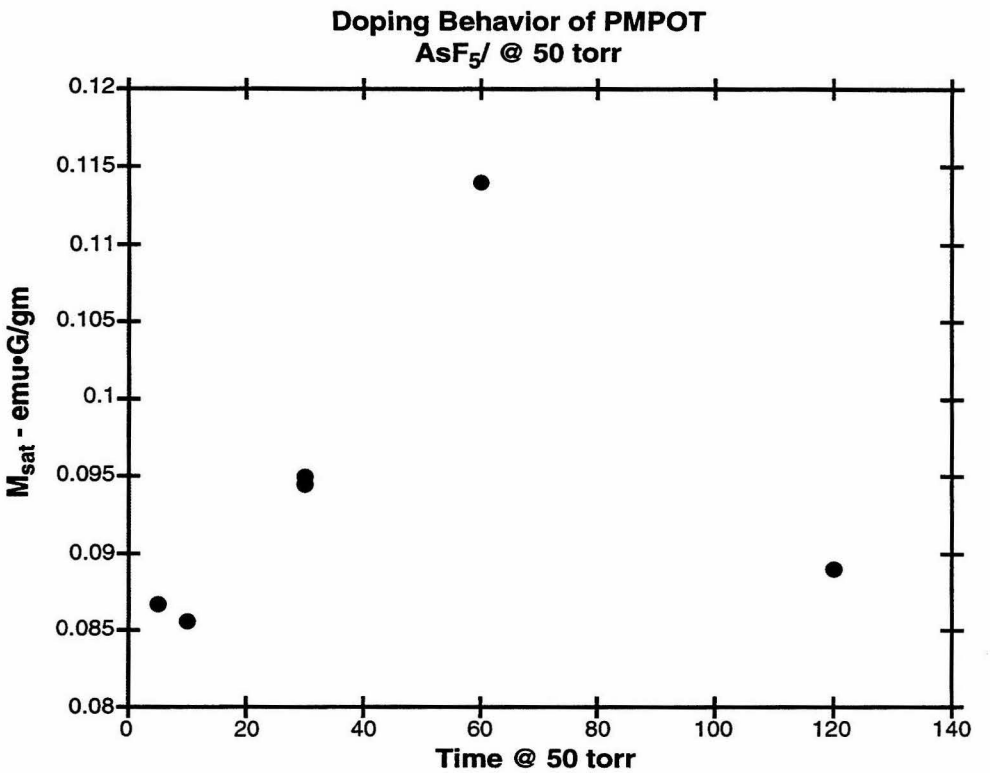



**Figure 2-10.** Variation of $M_{sat}$ (from saturation plot) versus length of exposure to $AsF_5$ at 50 torr for **PMPOT**.

Light $AsF_5$ doping on cast films typically yields $S$ values $\approx 2$ at 1.8 K with spin concentrations of only 0.2% (see Figure 2-11). Magnetization plots at 4.5 K give higher $S$ values ($S$ = 2.6 K). It is worth noting that both 1.8 K and 4.5 K plots yield the same $M_{sat}$ when $\chi_{dia}$ is taken from variable temperature data. We have interpreted this as meaning that there is little change in spin concentration by raising the temperature from 1.8 to 4.5 K. It is conceded, however, that $S$ and $M_{sat}$ are interdependent parameters and caution should be exercised when comparing Brillouin plots at two different temperatures. Other researchers consider $S$ to be independent of temperature in this regime and adjust the diamagnetic correction to ensure that this is so.[71] Very preliminary studies yielded $S$ values as high as 4.4 but these are considered to be unreliable as magnetization was only measured below $H/T \approx 2.5$ due to centering problems. Ideally the sample should be as close to saturation as possible to allow an accurate evaluation of $S$ values.

Prolonged $AsF_5$ doping increases the spin concentration to 2.6% but the $S$ value drops to 0.5 (Figure 2-12). It is highly likely that this material is extensively crosslinked. $AsF_5$ may readily oxidize benzene itself and indeed forms short oligomers of poly *p*-phenylene via this route (Figure 2-13). Such crosslinking is highly detrimental to our design as it destroys two spin sites at once and introduces random connectivity patterns.

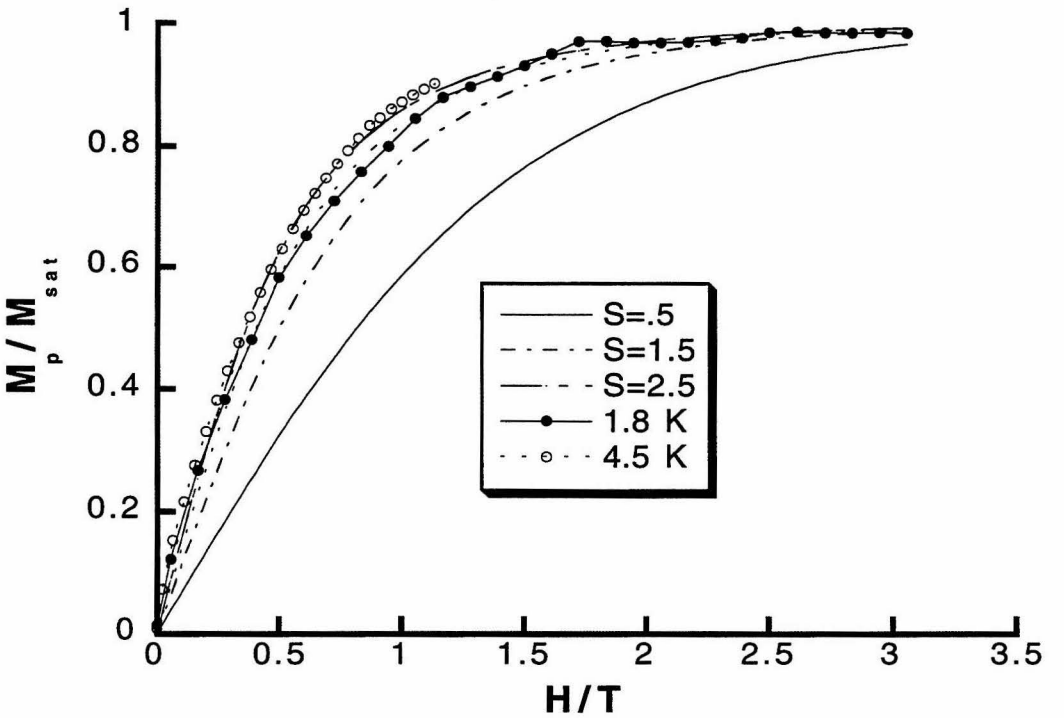



**Figure 2-11.** Magnetization behavior of PMPVTV (**1**) under $AsF_5$/light doping conditions, spin concentration = 0.2%. Measurements were conducted at 1.8 K(best fit $S$ = 2.1) and at 4.5 K (best fit $S$ = 2.6).

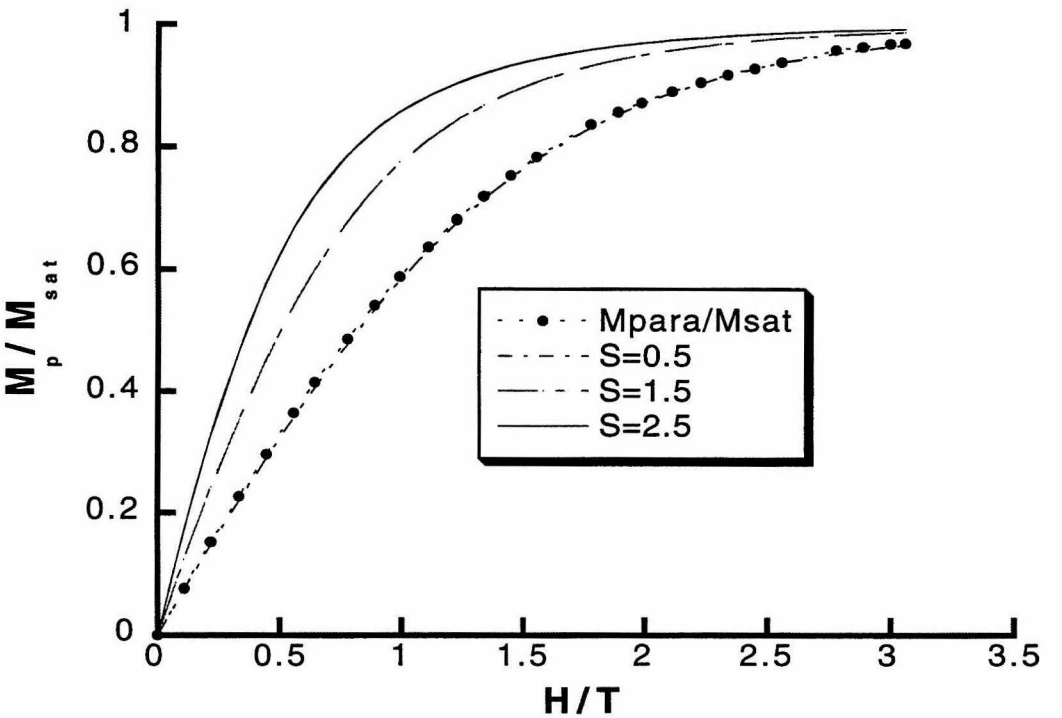



**Figure 2-12.** Magnetization behavior of PMPVTV (1) under $AsF_5$/heavy doping conditions at 1.8 K, best fit $S$ = 0.5 and spin concentration = 2.6%.

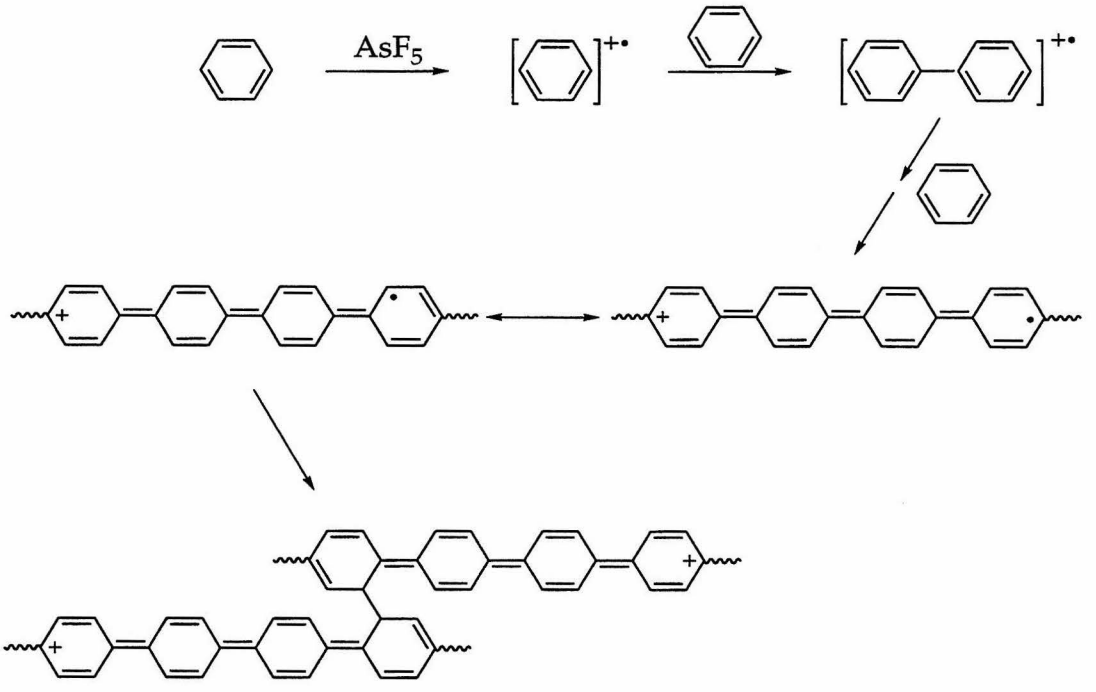



**Figure 2-13**. Schematic of synthesis and crosslinking of poly-*p*-phenylene by oxidation with $AsF_5$.

It was found in both doping protocols that the measured dopant uptake did not accurately reflect the number of monomers containing a spin. Lightly doped samples were typically 85% polymer by weight, heavily doped samples were typically 30-40% polymer by weight. The effect of polymer morphology was also briefly examined. It was found that *lightly* doped powdered samples of PMPVTV exhibited very similar magnetic behavior to *heavily* doped polymer films. The degree of dopant uptake in powdered samples is very difficult to control. Solution phase iodine doping studies were also conducted on this polymer. There was some attempt made to optimize the $I_2$ doping protocol, a constant concentration of polymer was stirred with excess $I_2$ for varying time lengths (30 minutes to 36 hours). Magnetic properties of this

material are not influenced much by the length of dopant exposure. Dopant uptake is rapid, spin concentration and *S* value remain roughly constant upon prolonged doping. Once again, dopant uptake does not accurately reflect measured spin concentrations. A typical data set is depicted Figure 2-14.

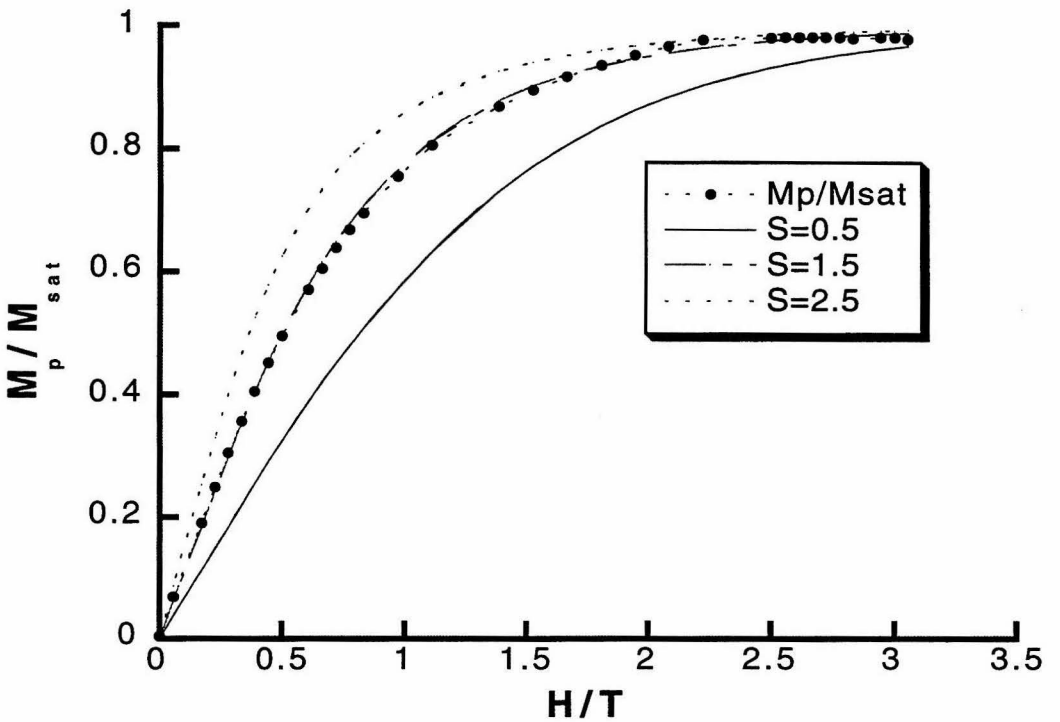



**Figure 2-14.** Typical magnetization plot of $I_2$-doped sample of PMPVTV (**1**), best fit S = 1.4 and spin concentration = 0.8%.

Iodine is a considerably milder oxidant than $AsF_5$, and it is reasonable to assume that unwanted crosslinking will be diminished as a consequence. $I_2$-doped PMPVTV shows only a 7% reduction in spin concentration when

allowed to stand at room temperature in an inert atmosphere for one week. This is an important criterion and **1** compares somewhat favorably to PMPOT which showed a substantial decay in spin concentration upon removal of dopant.[65] All doped samples of PMPVTV, however, were also insoluble in common organic solvents.

**Variable Temperature Behavior**

Fitting of magnetization data to the Brillouin function is a useful way of determining the spin state of a given material at a specific temperature. The measured *S* value, however, is often a composite of ferromagnetic and antiferromagnetic interactions, and these may be distinguished at some level by examining the magnetic susceptibility of the material as a function of temperature. Recall that our models for polaronic ferromagnets are designed to exhibit only *intramolecular* cooperative magnetic behavior in one dimension. *Intermolecular* interactions are anticipated to be antiferromagnetic in nature. A plot of relative effective moment versus temperature is a straightforward means of distinguishing between ferromagnetic and antiferromagnetic interactions. The moment is termed relative as the exact composition of the paramagnetic species in unknown; the units are arbitrary as a consequence. An upturn in the relative effective moment plot is indicative of ferromagnetic behavior whereas a downturn is characteristic of antiferromagnetic interactions. Both types of behavior are exemplified by a variable temperature plot of PMPVTV doped under $AsF_5$/light conditions (Figure 2-15). The downturn observed at 50 K is interpreted to represent the turn on of intermolecular antiferromagnetic interactions between polymer chains. Alternatively, the drop in effective moment may be a consequence of a $\pi$-$\pi$ dimerization. It has been

demonstrated that π-dimers may be an equally valid description of spinless conductivity in oxidized polythiophene.[73,74] In any event, the drop in effective moment means that *S* values measured at 1.8 K represent a lower limit to the "true" value. The moment remains roughly constant between 50 and 150 K, exemplifying Curie behavior in this region; this is consistent with the observation that a plot of $\chi_e$ versus inverse absolute temperature gives a straight line in this temperature range (see Figure 2-16). The moment drops again as the temperature increases to 200 K. This has been cautiously attributed to a turnoff of intramolecular ferromagnetic coupling as the high-spin preference is overcome by thermal energy. Although this phenomenon is observed in a reasonable temperature range,[75] the effect is subtle. The change in measured moment is very small at high temperature and data beyond 200 K is often very noisy for lightly doped samples. The paramagnetic susceptibility of these lightly doped samples approaches $10^{-10}$ emu•G at room temperature. This represents a lower limit of the MPMS measurement system using delrin sample holders. Other polymer samples that are nominally low-spin as evidenced by saturation plots at 1.8 K, exhibit a similar downturn at high temperature.[76]

May we estimate the extent of unwanted antiferromagnetic coupling in these systems? It has been determined that doped polymers generally fit a higher *S* value and especially so when *S* is significantly > $^1/_2$ at 1.8 K (See Figure 2-11). This is as expected, based on the effective moment plot of Figure 2-15. The measured *S* values are diminished by the weak antiferromagnetic interactions that become evident below 50 K. As the exact nature and distribution of spin sites in these systems is unknown, extraction of exchange energies, *J*, from the Bleaney-Bowers and Van Vleck equations[70] is of limited value. It is valid, however to compare two different relative effective

moments $\mu_1$ and $\mu_2$ at two different temperatures $T_1$ and $T_2$, using relationships (5) and (6). Typically, the maximum value of $\mu_{eff}$ ($\mu_{eff}^{max}$) is larger than the low temperature value ($\mu_{eff}^{LT}$) by only about a factor of $\frac{4}{3}$. Since

$$\mu_{eff} = \sqrt{g^2 S(S+1)} \tag{5}$$

then

$$\frac{\mu_{eff}^{max}}{\mu_{eff}^{LT}} = \sqrt{\frac{S^{max}(S^{max}+1)}{S^{LT}(S^{LT}+1)}} = 1.33 \tag{6}$$

For a typical case with $S^{LT}$= 2.5, one obtains $S^{max}$≈3.5. This is a significant difference, but not one that leads to any qualitative changes in interpretation.

It may well be that the drop in moment is also due to spin dimerization or other such phenomena, but we cannot distinguish between the two possibilities as the quantities *N* and *S* are inseparable in these systems. The important point, however, is that these intermolecular antiferromagnetic interactions in polymer samples are *weak* in nature and may be quantified by comparing the relative effective moments at different temperatures. Small molecules studied in this group do exhibit far stronger interactions in the solid state at low temperature as evidenced by dramatic drops in the effective moment plot.[77,78] It is conceivable that π-stacking and other mechanisms for antiferromagnetic interaction between spin sites are less prevalent in macromolecular systems because of their amorphous nature. It has been suggested that dilution in a diamagnetic matrix may diminish intermolecular coupling further.[76]

The weak nature of these through-space antiferromagnetic interactions is emphasized by the Curie-Weiss behavior of PMPVTV. Recall that

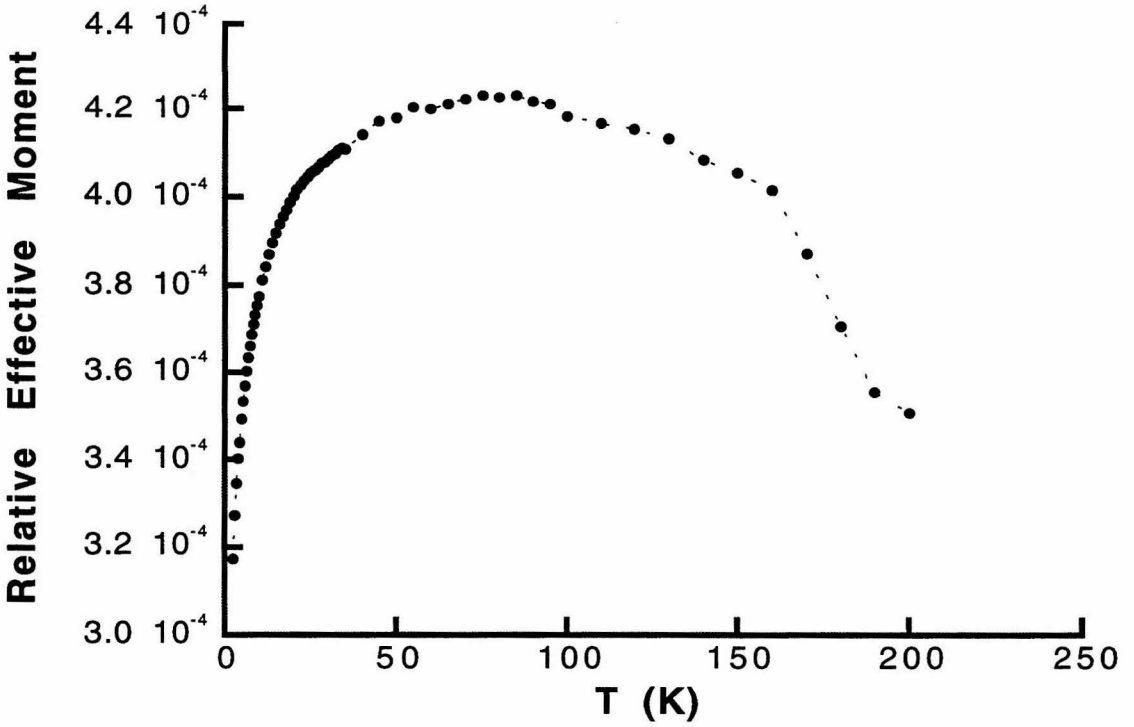



**Figure 2-15.** Plot of relative effective moment versus absolute temperature for lightly doped PMPVTV (**1**). Effective moment is in arbitrary units.

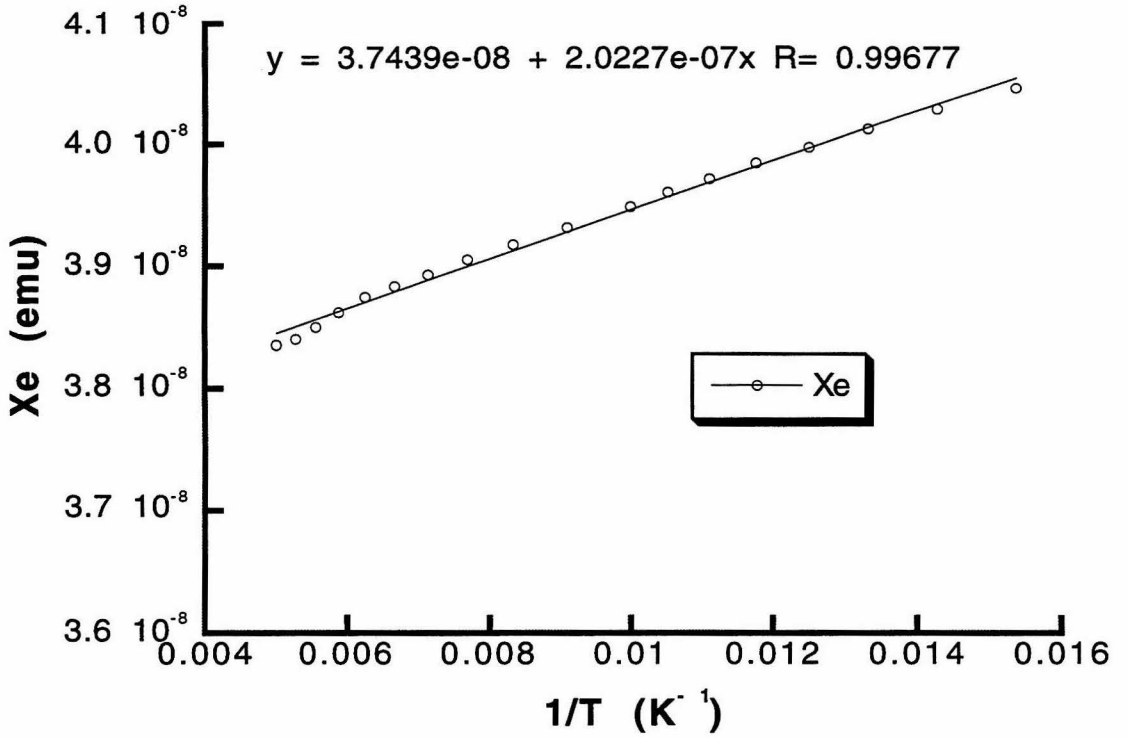



**Figure 2-16.** Plot of total magnetic susceptibility, $\chi_e$, versus inverse absolute temperature for between 50 and 200 K. Data are for PMPVTV (**1**) doped under $AsF_5$/light conditions.

$$\chi_p = \frac{C}{T - \theta} \tag{7}$$

which upon rearranging gives

$$\frac{1}{\chi_p} = T\left[\frac{1}{C}\right] - \frac{\theta}{C} \tag{8}$$

Thus, at sufficiently high temperature, $T \geq 10\theta$, a plot of inverse paramagnetic susceptibility versus temperature yields a straight line with slope $1/C$ and intercept $\theta/C$. Thus, high temperature susceptibility measurements in the Curie region are used to analyze magnetic interactions between particles at low temperature. Positive values of $\theta$ imply ferromagnetic coupling whereas negative $\theta$ values are indicative of ferromagnetic coupling. PMPVTV and all other doped polymers discussed in this work have small negative Weiss constants (see Figure 2-17), consistent with weak antiferromagnetic coupling at low temperature. It is concluded that these weak through space interactions are of limited importance in these systems.

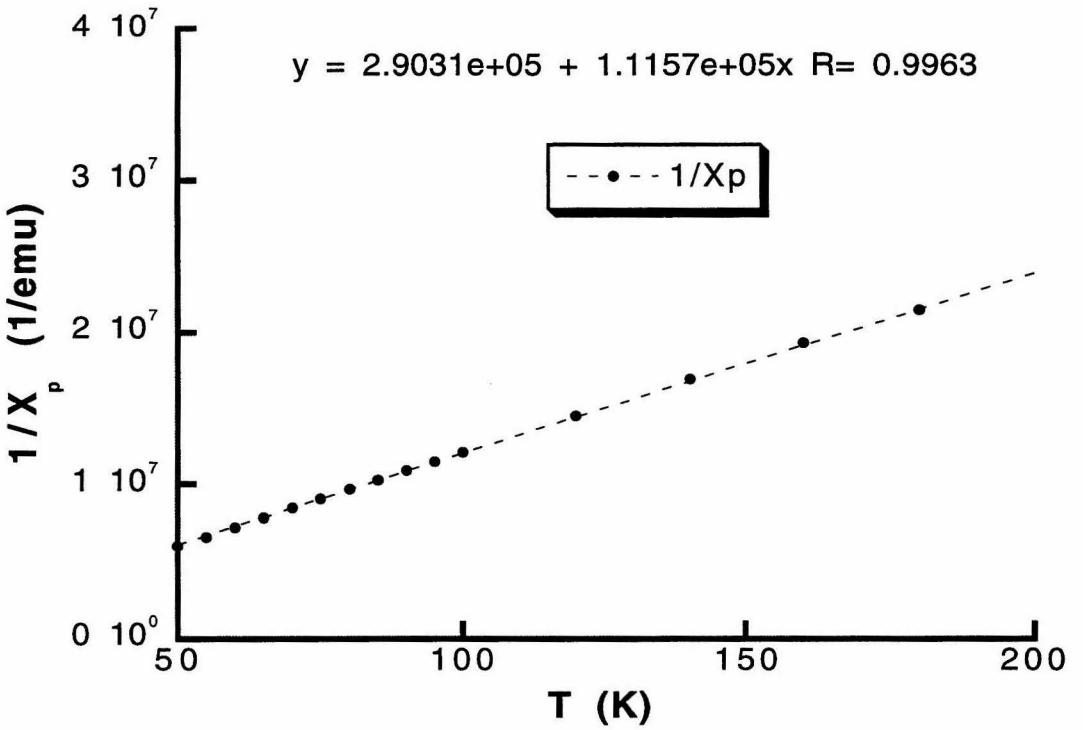



**Figure 2-17.** Plot of inverse paramagnetic susceptibility versus absolute temperature for heavily doped PMPVTV (**1**). The Weiss constant, $\theta \approx -0.38$ K.

**PMPT, 2**

**Iodine Doping**

Initial results from PMPVTV were encouraging as they validated our paradigm for polaronic ferromagnetism in a new system. The magnetization behavior of PMPVTV and PMPOT, however, are very similar and it was unclear how the model may be improved. Bipolaron formation has always been a concern of ours and PMPT was designed to address this issue. The conjugation length of the SC is minimal in this system, consisting only of an isolated thiophene ring. Its optical absorption maximum ($\lambda_{max}$ = 345 nm) still compares favorably with Poly (3,4-diisopropylidenecyclobutene), **3**, ( ($\lambda_{max}$ = 278 nm), a polymer dopable with $I_2$. There is a subtle difference between PMPT, PMPTT versus PMPVTV and PMPOT. In the former class, the solubilizing group is tetradecyl whereas in the latter it is octadecyloxy.
The length of the alkyl chain should not be important but the presence of oxygen could be. It is unlikely that oxygen contributes to polaron stability given its *meta* position but it highly likely that aryl ethers are cleaved with strong Lewis acids such as $AsF_5$.[79]

PMPT, however, did not generate a significant number of spins when exposed to solution phase $I_2$ (Figure 2-18). There was, however, a noticeable weight uptake of dopant (≈ 10%) which may reflect mere adsorption of dopant onto the polymer surface. There was no apparent physical change upon doping this system. The polymer could be redissolved in methylene chloride or chloroform, behavior not observed in PMPVTV or PMPOT. It is concluded that the conjugation length of PMPT is too small to be oxidized under mild conditions. Conductivity observed in **7** may well be due to a mechanism other than polaron/bipolaron formation.[22,23]

**$AsF_5$ Doping**

PMPT was cast a thin film and exposed to $AsF_5$ in the same manner as PMPOT. A variety of doping conditions were attempted none of which produced a material with *S* significantly greater than 0.5 (Table 2-3). Doped material was brittle and insoluble in common organic solvents. It is apparent that spin concentration is highly dependent on sample morphology. Such variability is not entirely unexpected in two phase doping of this nature. This protocol was less emphasized in later studies.

**Alternative Dopants**

A number of other solution phase doping studies were performed on this polymer. Nitrosonium tetrafluoroborate reacted vigorously with PMPT in anhydrous $CH_2Cl_2$ as evidenced by the rapid evolution of brown fumes upon mixing of the two reagents in an inert atmosphere. The doped polymer exhibited a spin concentration of approximately 2% and S = 0.7. Silver tetrafluoroborate appeared to react with PMPT as evidenced by the deposition of metallic silver. The doped material appeared to remain soluble and formed a film upon removal of the solvent. The spin concentration, however, was approximately 0.5% and *S* = 0.5.

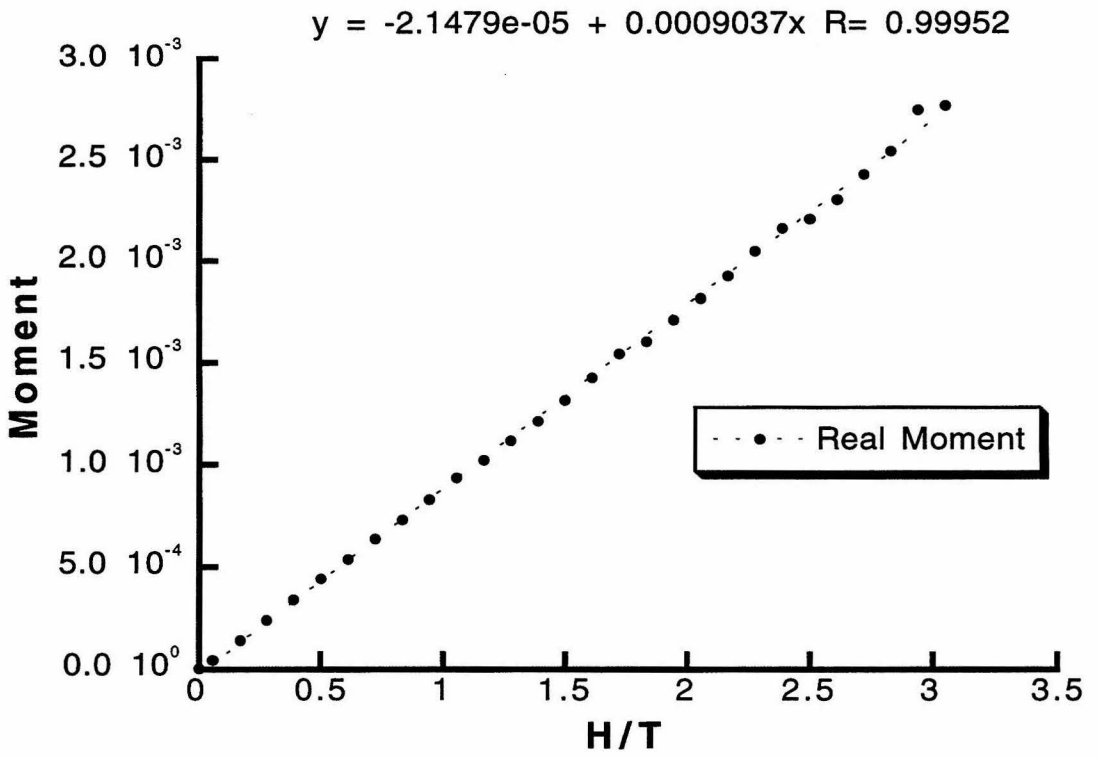



**Figure 2-18.** Plot of moment versus *H/T* for solution-phase $I_2$-doped PMPT (**2**). Note that the intercept is actually a *negative* number implying a negligible spin concentration.

| Sample Morphology | Pressure/ Time | Msat emu•G/g | Spin concentration | S |
|---|---|---|---|---|
| powder | 15 torr/10 min | 0.69 | 4.3 | 0.6 |
| powder | 5.0 torr/10 min | 0.12 | 1.0 | 0.5 |
| film | 75 torr/30 min | 0.03 | 0.2 | 0.6 |
| film | 75 torr/30 min | 0.11 | 0.8 | 0.6 |
| powder | 4.2 torr/ 5 min | 0.34 | 2.6 | 0.5 |
| film | 175 torr/ 7 hours | 0.40 | 6.5 | 0.6 |

**Table 2-3.** Values of $M_{sat}$, $S$, and Spin Concentration as percent monomers doped for PMPT (**2**) exposed to varying pressures of $AsF_5$. Measurements were conducted at 1.8 K.

**Variable Temperature Behavior**

The variable temperature behavior of PMPT mimics that of PMPVTV. There is a downturn in the effective moment plot at ca. 50 K. A representative effective moment plot of an $AsF_5$-doped sample of PMPT is shown in Figure 2-19. The change in effective moment upon going from low temperature to high temperature is again very small (≈ 10-30%) emphasizing the weak nature of antiferromagnetic coupling between polymer chains.

There is a possible drop in the moment beyond 200 K in some samples but this did not prove to be very reproducible in this system under $AsF_5$ doping conditions; the moment actually rose again in some cases beyond 200 K. This irreproducibility was independent of spin concentration and underscores the need for caution in interpreting data in this high temperature regime.

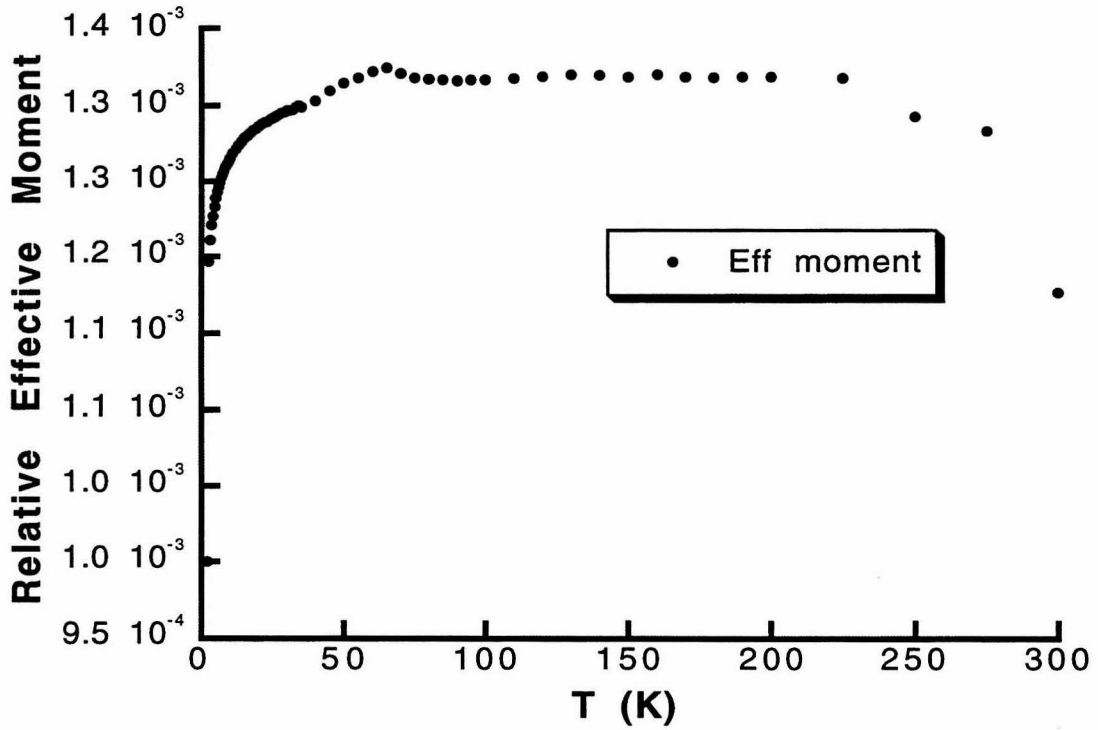



**Figure 2-19.** Relative effective plot of a powdered sample of PMPT (**2**) doped with $AsF_5$ at 15 torr for 15 minutes.

**Thermal Spin Stability**

A feature that distinguishes PMPT from all other polymers discussed here

is the very poor thermal stability of spins generated. In contrast to PMPVTV or PMPOT, this material loses its magnetization rapidly even in an inert atmosphere in the absence of excess gaseous dopant. A lightly doped $AsF_5$ sample lost 90% of its magnetization upon standing for three days in a nitrogen-filled glovebox in a sealed tube. This observation demonstrates the remarkable ability of oxidized polymer samples to react with each other in the solid state. In addition, it is consistent with the cross-conjugated nature of the meta toplology. Spins generated are unable to achieve greater stability by delocalization through the $\pi$-system.

**PMPTT, 3**

PMPTT is a close cousin of PMPVTV and demonstrates similar behavior upon doping with $I_2$ in the solution phase. It does, however, exhibit some minor variability in its magnetization behavior when doped with $I_2$. This may be a function of different particle sizes. *S* values as low as 0.8 and as high as 1.2 were observed; *S* values close to 1 and spin concentrations of the order of 1% are typical. PMPTT is sparingly soluble in organic solvents, cannot be cast as a thin film and was doped as a powder in iodine solution. No correlation could be made between changes in spin concentration, *S* and length of doping time. Plots of effective moment against temperature also showed some variability, the ratio of low temperature to high temperature effective moments were in the range of 10-40%, and had no obvious correlation with *S* or spin concentration. The downturn was seen consistently, however, at ca. 50 K.

Heterogeneous gas phase $AsF_5$ doping was conducted on a loose powder. Significant spin concentrations were observed but *S* values close to 0.5 were obtained using both light and heavy doping protocols. Dopant uptake in

these powder samples is very rapid and difficult to control so comparisons to thin film measurements are dangerous. The results are briefly summarized in Table 2-5.

| Dopant | Doping Time | $M_{sat}$ (emu•G/g) | Spin Concentration | $S$ |
|---|---|---|---|---|
| $I_2$ | 24 hours | 0.04 | 0.5 | 1.4[a] |
| $I_2$ | 6 hours | 0.18 | 1.8 | 0.8 |
| $I_2$ | 5 hours | 0.1 | 1.0 | 1.0 |
| $I_2$ | 5 hours | 0.09 | 0.9 | 1.0 |

[a]Limited data set, poorer fit to Brillouin function.

**Table 2-4.** Values of $M_{sat}$, $S$, and spin concentration as percent monomers doped for $I_2$-doped PMPTT (**3**) measured at 1.8 K.

| Doping Conditions | $M_{sat}$ (emu•G/g) | Spin Concentration | $S$ |
|---|---|---|---|
| $AsF_5$ (45 torr/30 min) | 0.62 | 8.8 | 0.6 |
| $AsF_5$ (200 torr/5 h) | 0.86 | 18.1 | 0.7 |
| $AsF_5$ (5 torr/5 min) | 0.86 | 9.8 | 0.7 |

**Table 2-5.** Values of $M_{sat}$, $S$, and spin concentration as percent of monomers doped for $AsF_5$-doped PMPTT (**3**) measured at 1.8 K. Dopant pressures and exposure time lengths are noted in parentheses.

**Thermal Stability**

PMPTT shows moderately good thermal stability when doped. $I_2$-doped material showed a 6% decrease in spin concentration when allowed to stand in the glovebox for thirty six hours. A sample doped heavily with $AsF_5$ showed an 80% reduction in spin concentration when allowed to stand in the glovebox for 10 days. In terms of stability, PMPTT may be considered to be intermediate between PMPT and PMPVTV.

**PMPVTTV, 4**

The magnetic properties of this material differ substantially from the other three when doped under the same conditions. Introducing this very large dopable segment into the polymer backbone increases the spin concentration considerably upon iodine doping. This is not entirely surprising as more conjugated SCs are expected to be more easily oxidized. In contrast to the other thiophene-based polymers, however, spin concentration actually *decreases* upon prolonged $I_2$ doping. Three separate runs were performed.

| Dopant Exposure/hours | Spin Concentration | $S^a$ |
|---|---|---|
| 0.5 | 2.2 | 0.5 |
| 6 | 1.3 | 0.6 |
| 22 | 0.6 | 0.7 |

[a]This small apparent increase in $S$ can be accounted for entirely by 10 ppm of iron detected by SQUID magnetometry. The $S$ value is essentially unchanged upon correction (see later discussion).

**Table 2.6.** Plot of spin concentration (expressed as percent monomers doped) and $S$ value of PMPVTTV (**4**) as a function of iodine doping time.

PMPVTTV may be cast as a somewhat brittle film from $CHCl_3$. No evidence of ferromagnetic coupling amongst polarons is apparent when the material is doped using light or heavy doping $AsF_5$ protocols. Spin concentrations and *S* values are unexceptional: spin concentrations for lightly and heavily doped samples are 1.3 % and 5.5% respectively. The *S* value is close to 0.5 in both instances, and more extensive studies were not performed. Variable temperature behavior is similar to other thiophene systems studied.

**Electrochemical Behavior and Chemical Reversibility**

In principle, doped conducting polymers may be treated with a compensation agent such as $NH_3$ or $Na_2S_2O_3$ to remake soluble diamagnetic polymers. Treatment of iodine doped thiophene polymers with aqueous $Na_2S_2O_3$ failed to solubilize a significant amount of material. None of the thiophene polymers demonstrated a reversible redox wave when analyzed by cyclic voltammetry. A cast film of PMPVTV has an irreversible redox wave at approximately 1.1 V versus SCE, consistent with recent studies on model thiophene oligomers.[80-83] PMPVTTV has an irreversible oxidation wave centered at approximately 0.8 V versus Ag/AgCl which disappears after one cycle(Figure 2-20).

**Discussion and Overview**

Meaningful insights may be obtained by comparing the magnetic data obtained from these thiophene systems and indoloindole-based polymers[69] also synthesized in this group (Table 2-7). Early studies by Hünig[84] established that the large heterocyclic indoloindole systems form an especially stable radical cation. This manifests itself in large spin concentrations and exceptional thermal stabilities upon oxidation with iodine. Interestingly,

expansion from PMPII to PMPVIIV results in a substantial decrease in spin concentration and $S$ value; this probably reflects dication formation. $S$ values $\approx 0.9$ are observed for the parent PMPII system, and its variable temperature behavior has recently been reexamined by the author. An unmistakable upturn in the effective moment attributed to ferromagnetic coupling between polarons is observed at 50 K, peaking at 5.5 K whereupon the moment drops again, presumably due to antiferromagnetic interactions. It is noted that the effects are subtle: the absolute change in moment from low to high temperature is less than 6%, but is undoubtedly real given the absolute size of the moment in this sample. If the ratio of low to high effective moments is a reasonable measure of undesirable antiferromagnetic interactions, then these are even smaller in this system than its thiophene analogs. An electrochemically doped sample of PMPF diluted in a diamagnetic matrix has been extensively studied and shows similar variable temperature behavior, i.e., an upturn in effective moment beginning at 30 K which peaks at 3-5 K. A comparison of effective moment ratios at low and high temperature (ca. 10%) suggest that through space antiferromagnetic interactions in this material are similar to all other *polymeric* models for the polaronic ferromagnet.[76]

How can we rationalize high $S$ values in PMPVTV and PMPOT? Doping in these systems is heterogeneous in nature. This is particularly the case for two-phase systems such as $AsF_5$ interacting with a polymer film. The notion that doping does not produce homogeneous materials has considerable precedent in the conducting polymer field[15,16] and may explain why $AsF_5$/light samples give higher $S$ values than $I_2$-doped samples. PMPVTV, for example, gives $S \approx 2$ and yet spin concentration is only 0.2%. Less than one in every 100 monomers is spin-containing! We believe that these samples contain islands of heavy doping that can apparently produce large $S$

values. As iodine doped samples are insoluble upon removal of solvent, it is likely that the polymer precipitates as doping proceeds. Solution phase doping studies of thiophene systems were performed at constant concentration and no attempt was made to optimize this variable. Indeed, it may be argued that insolubility has some benefits: radical sites may be more stable in the solid state versus solution especially as oxidation waves for **1-4** are irreversible.

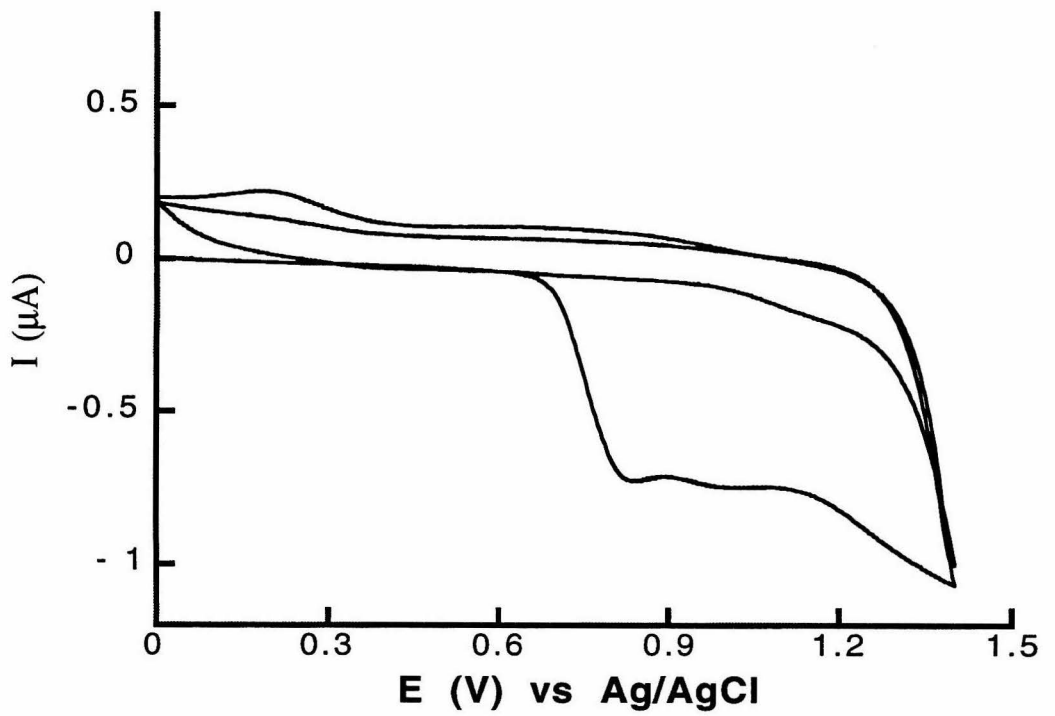



**Figure 2-20.** Cyclic voltammogram for the oxidation of PMPVTTV(**4**) in $CH_2Cl_2$/ 0.1 M $Bu_4NClO_4$, $\nu$ = 100 mV/s.

| Polymer | $I_2$ | $AsF_5$ | |
|---|---|---|---|
| | | light | heavy |
| PMPOT (15) | 1.4 (0.6%)[b] | 2.2[c] (0.5%) | 0.5 (3.6%) |
| PMPVTV (1) | 1.4 (0.8%) | 2.1[d] (0.2%) | 0.5 (2.6%) |
| | | 2.6[d] (0.2%)[e] | |
| PMPVTTV(14) | 0.5 (2.2%) | 0.6 (1.3%) | 0.6 (5.5%) |
| | 0.6[e] | | |
| PMPT (2) | –[f] | 0.6 (0.6%) | 0.6 (6.5%) |
| PMPTT (3)[d] | 1.0 (1.0%) | 0.6 (8.8%)[g] | 0.7 (18.1%)[g] |
| PMPVIIV | 0.5-0.6 (16-17%) | –[h] | –[h] |
| PMPII | 0.8 (32%) | –[h] | –[h] |
| | 1.0 (32%)[e] | | |

[a] Measurements at 1.8 K unless noted otherwise

[b] Gas phase $I_2$ doping. Solution doping produces essentially identical results.

[c] Values as high as 4.0 have been seen.

[d] Values as high as 4.5 have been seen.

[e] 4.5 K

[f] No significant moment

[g] Powder sample rather than film for $AsF_5$ studies

[h] Not performed

**Table 2-7.** Values of $S$ and spin concentration as % monomers doped[a]

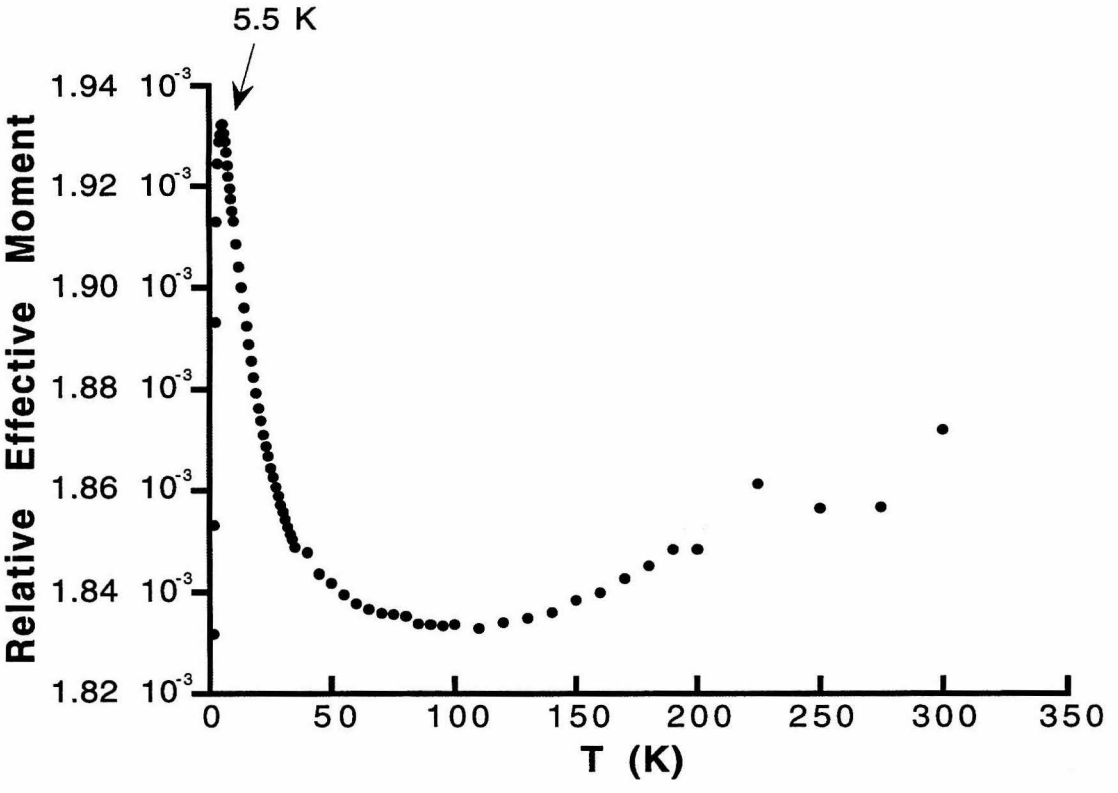



**Figure 2-21.** Plot of relative effective moment versus temperature for $I_2$-doped PMPII.

The interpretation of variable temperature data depicted in 2-17 for PMPVTV must now be reevaluated in the light of results obtained from PMPF and PMPII. The latter two systems show a definite rise in the effective moment plot at low temperature. Spin density at the benzylic position of PMPVTV is estimated to be considerably larger than in PMPF and PMPII. A simple Hückel analysis of spin density patterns and scaling the calculated single-triplet gap of *meta*-xylylene (10 kcal/mol)[27] suggests that the onset of

ferromagnetic coupling in PMPVTV would be observed in the 200-300 K region. Data in this temperature range is often noisy because temperature fluctuations of the MPMS become more significant for small paramagnetic susceptibilities. Given the low spin concentrations of PMPVTV and PMPOT, an apparent rise in effective moment at 200 K cannot be unambiguously assigned to an onset of intramolecular ferromagnetic coupling and may well be due to another effect.

**Ferromagnetic Coupling and Impurities**

The magnetization behavior of control polymers PPPV and PPPOT has been examined in early studies. Unlike the early prototype for the polaronic ferromagnet PMPOT, there is no rationally designed ferromagnetic coupling pathway in these *para*-linked systems and no significant cooperative behavior between spins was anticipated. *S* values close to 0.5 were observed in these systems when doped under the same conditions as PMPOT. Moreover, PPPV when doped with iodine, gives S ≈ 0.5 *with similar spin concentrations* as its *meta*-linked analog, PMPOT. No further controls were performed on thiophene-based systems but an examination of the data summarized in Table 2-7 does suggest that the series is self-checking at some level. Polymers doped to similar spin concentrations under the same conditions do not give the same *S* values. An evaluation of the extent of ferromagnetic impurities using SQUID magnetometry was performed on these systems. A plot of $\chi_p$ versus *1/H* yields a straight line at high temperature. The slope of the line is equal to the magnetization due to ferromagnetic impurities. In only one instance, iodine-doped PMPVTTV, was a significant concentration of iron (10.2 ppm) observed. Ferromagnetic impurities, if present in $AsF_5$-doped PMPVTV, were below the limit of detection of the MPMS.

**Conclusions and Outlook**

A refined understanding of the polaronic ferromagnet paradigm has emerged from these studies. A number of important conclusions may be made from this work:

- Suitable prototypes for the polaronic ferromagnet may be synthesized in a reliable manner employing a highly efficient Suzuki cross-coupling reaction. Reaction conditions are mild and yields are generally excellent. This new synthetic strategy broadens the scope of candidates for the SC component and represents a significant improvement over Wittig polymerization protocols.

- *S* values significantly greater than 0.5 were demonstrated for PMPVTV and PMPTT, close relatives of the original prototype of the polaronic ferromagnet, PMPOT, further extending the validity of the polaronic ferromagnet paradigm.

- Higher spin concentrations are obtained with more delocalized SCs. This observation validates at some level the bipolaron suppression mechanism for *meta*-linked systems proposed in Figure 2-5. Iodine-doping studies of PMPT establish a minimum conjugation length for mild solution phase doping. Very short dopable segments generate highly unstable polarons upon oxidation by caustic $AsF_5$. Thermal stability of $AsF_5$-doped materials roughly scales with conjugation length of the SC.

- Undesirable *intermolecular* antiferromagnetic coupling is roughly independent of spin concentration, sample morphology, doping method and *S* value; it is weak in magnitude for all polymeric systems studied.

Limitations in the systems' design have also been exposed in this work most notably:

- Limited solubility of doped polymeric systems in organic solvents.

- Low spin concentrations in some instances.
- Inaccessibility to electrochemical doping methods.
- Low *S* values for highly delocalized SCs.

Some of the shortcomings listed above are interrelated: neutral polymers are typically soluble in methylene chloride, chloroform, toluene, benzene and THF. Polycationic species, however, only dissolve in highly polar solvents such as DMF, DMSO, acetonitrile or, in exotic cases, water. Polyanionic systems may be dissolved in lower dielectric solvents in some instances. As previously mentioned, PMPF may be successfully bulk electrolyzed in THF using $Bu_4NClO_4$ as electrolyte to form a soluble polyanion; this represents a major technological advance in this field as a measurable amount of charge may be delivered to the polymer. Insoluble, chemically doped samples, however, are less well characterized and are susceptible to overdoping and underdoping. The choice of electrolyte is important in electrochemical doping as it is the source of the counterion. Tetralkylammonium salts are relatively lipophilic and readily available. Typical electrolytes suitable for bulk oxidations of polymers include $LiClO_4$, $NH_4PF_6$, and $NaBF_4$, none of which improve solubility of radical cations in a low dielectric solvent.

In light of the above, some important questions need to be addressed.

- Do radical cations have any advantages over radical anions?
- Can the solubility problems of polycations be resolved?

Initial studies focused on cations as the conducting polymer field is dominated by readily oxidized (*p*-type) materials such as polythiophene, polypyrrole and polyacetylene. Most anions have reduction potentials below 0 V and are susceptible to air oxidation, whereas polycations are less reactive and are often stable in ambient conditions. Hence, it is more likely that any technologically useful polaronic high-spin organic material will be

polycationic in nature.

Solubility issues remain a stumbling block and literature precedent for planar, conjugated polymers soluble in high dielectric solvents is sparse. It has been demonstrated that polythiophene substituted with a polyether chain is insoluble in acetonitrile but may be dissolved when mixed with $LiBF_4$.[85] The oxygens on the polyether presumably chelate the small metal cation (Figure 2-22).

A suitable polyether-substituted thiophene derivative, **36**, for the polaronic ferromagnet has been synthesized as outlined in Schemes 2-7 and 2-8. Oligoether-substituted polythiophenes have been polymerized to high molecular weight in DMF.[86]

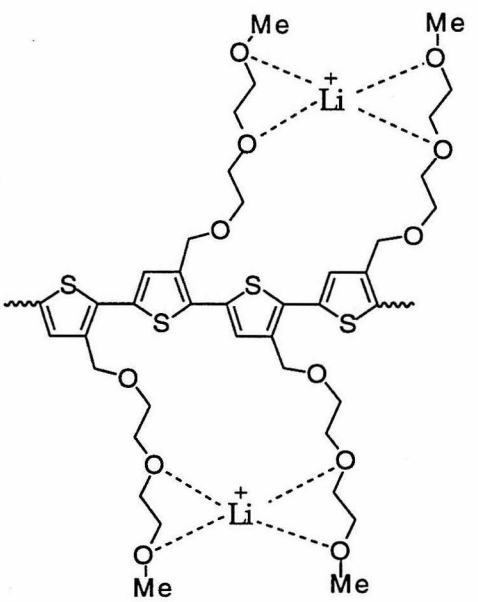
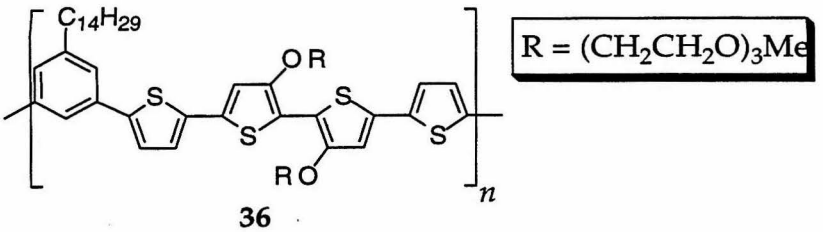
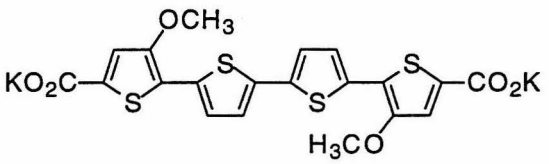



**Figure 2-22.** Solubilization of a oligoether-substituted polythiophene derivative when mixed with $LiBF_4$ in acetonitrile.




**36**

The radical cation of **37** can be generated bulk electrolysis in *aqueous media* in the absence of any added electrolyte. Compensation with $Na_2S_2O_3$ regenerates the neutral species in over 90% yield.[87] Additional studies suggest that changing the position of "inside" methoxy groups on the quaterthiophene backbone does not perturb the electronic structure much.[88,89] Thus, a bismethoxy quaterthiophene was chosen as a suitably stable SC to address solubility concerns. Incidentally, a recent publication suggests that dimethoxy terthiophene derivatives also yield very stable radical cations;[90] this system is a more attractive target because of its compact nature.

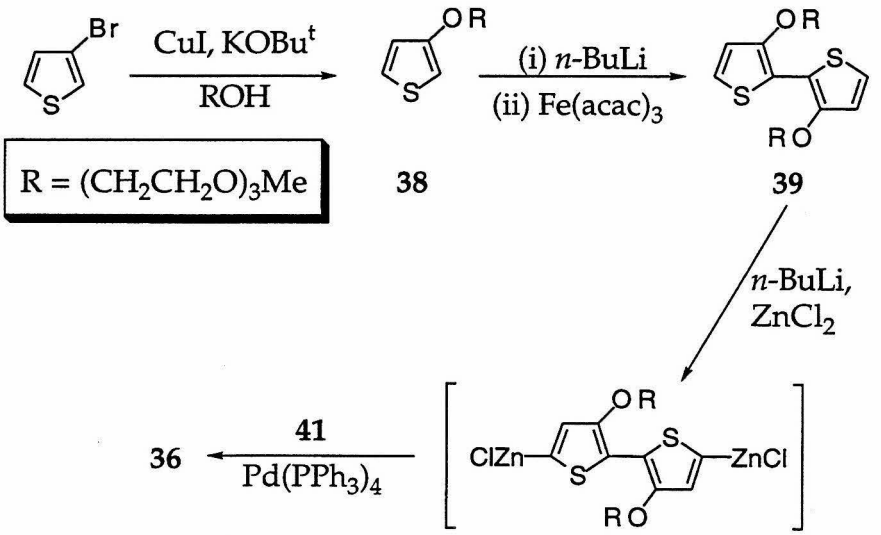



**37**

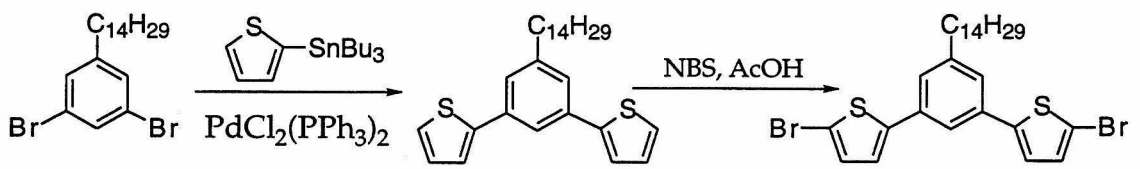
Unfortunately, neither dihalide nor diorganostannane derivatives of bisalkoxy 2,2'-bithiophenes are stable and an *in situ* polymerization protocol must be employed.[91] An initial attempt yielded a material of molecular weight 2500-4000, indicative of three to five monomer units per polymer chain. The resulting material was insoluble in DMF and acetonitrile. Addition of $LiClO_4$ did not improve solubility. The material may, however, be dissolved to at least 3 mM concentration in a 1:4 $CH_2Cl_2$:DMF mixture in

the presence of $LiClO_4$ (ca. 0.3 M). It is likely that the material may be electrolyzed in this solvent/electrolyte mixture. The anodic limitations of DMF versus acetonitrile, however, are noted.[92] Time restrictions did not permit an evaluation of the magnetic properties of doped **36**.

**Scheme 2-7**




**Scheme 2-8**



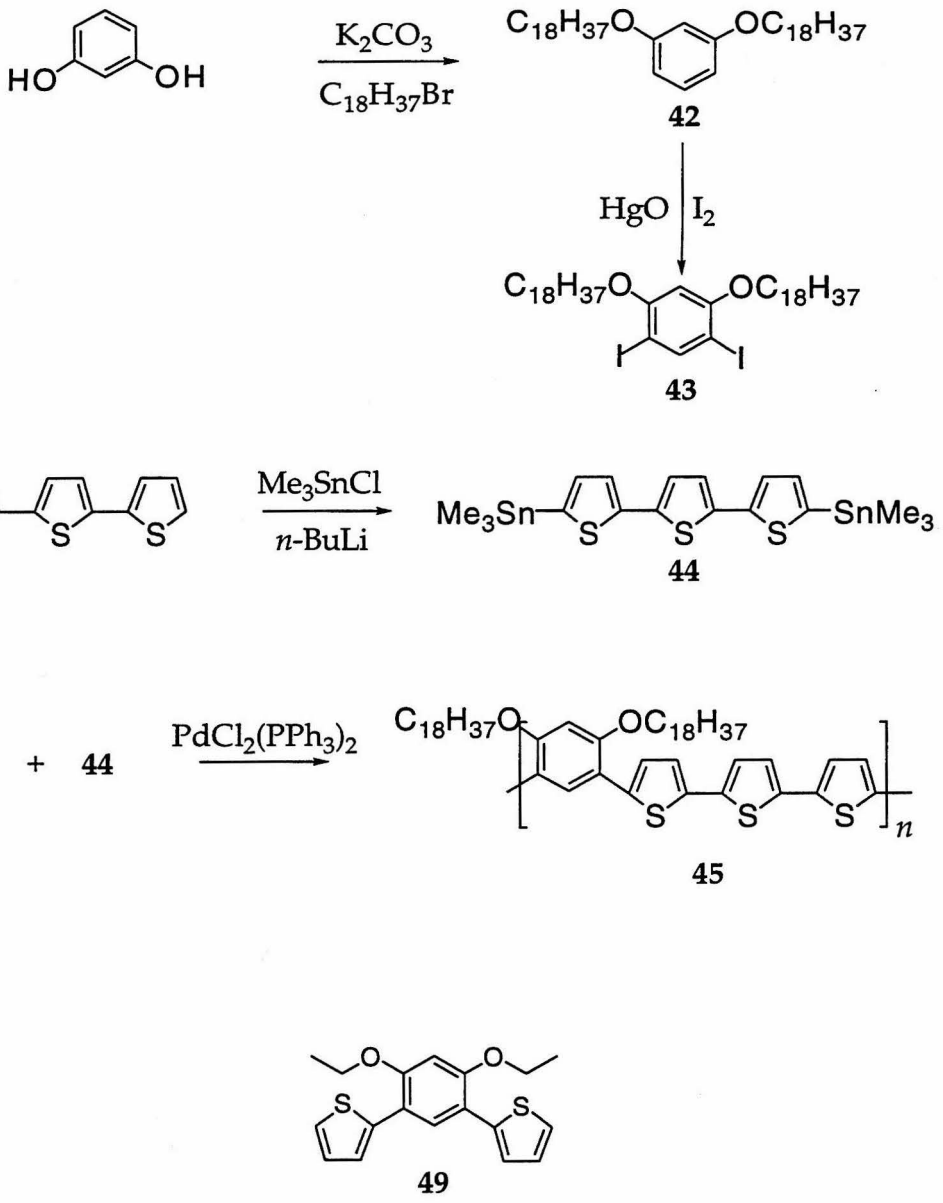

It is the author's opinion, however, that water solubility should remain a target. High spin concentrations may be obtained by electrolysis in organic

solvents but doped polymer cannot be separated from electrolyte. This imposes several technological limitations on the system, most notably a substantial reduction in $M_{sat}$ in terms of emu•G/g of material. In addition, desirable properties such as thin film formation are lost upon mixing a polymer in a diamagnetic matrix. Water, however, due to its high dielectric constant, may serve as a medium for bulk electrolysis *in the absence of added electrolyte*. Both Suzuki[57] and Stille couplings[93] have been conducted successfully in water using modified water-soluble palladium catalysts. "Self-doped" conducting polymers are attracting increasing interest.[94-96]

**Increasing *S* and Ferromagnetic Coupling Strength**

Our schematic design for high-spin materials depicted in Figure 2-1 describes the SC and FC as discrete units. Spin delocalization into the FC is possible, however, so this designation is somewhat arbitrary. It may be argued that such delocalization is beneficial as it increases polaron stability without sacrificing spin density at the benzylic position. This can easily be promoted in cationic systems by simply attaching alkoxy sidechains *ortho* to the SC. Some synthetic progress has been made in this area as outlined in Scheme 2-9. Twisting of the polymer backbone is obviously a concern but should be less of a problem for five-membered rings. Geometry optimization of a model system **49** at the AM1 level,[97] as implemented in the program SPARTAN,[98] suggests that the dihedral angle of the neutral species is only 30°. This assertion is supported by optical absorption data of **45** (see Experimental section). The radical cation is calculated to be planar.

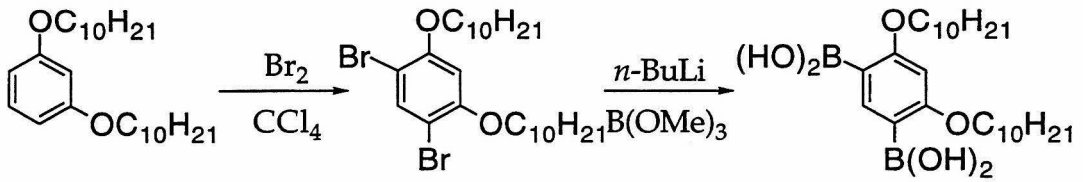
**Scheme 2-9**




It has been found that alkoxy-substituted bisboronic acids, e.g., **48**, whose synthesis is outlined in Scheme 2-10, cannot be purified as their catechol or glycol esters. Reaction of the free acid with 5,5'-Dibromo-2,2'-Bithiophene, **35**, under standard Suzuki coupling conditions yielded only oligomers. This

observation is consistent with limitations of the Suzuki reaction described recently.[55] Stille coupling is a moderately successful method of polymerizing diiodobisalkoxy benzene derivatives and is utilized here.[99]

**Scheme 2-10**




**46** **47** **48**

**The Role of Defects**

Even under the best of circumstances, it is unreasonable to assume that a given system will be defect free. Possible defects include undoped or overdoped (bipolaronic) segments, and products of radical decay. These defects are highly detrimental to these systems as adjacent spins are insulated from each other. A reasonable solution to this problem is crosslinking of polymer chains. 1,3,5-trisubstituted benzenes can also high-spin couple three SCs.[5,6,100,101] Such a topology provides alternate paths and may help to diminish the effect of interchain antiferromagnetic interactions. Highly crosslinked polymers, however, are typically insoluble and limitations of this strategy are discussed briefly in an appendix describing studies on crosslinked pyrrole systems.

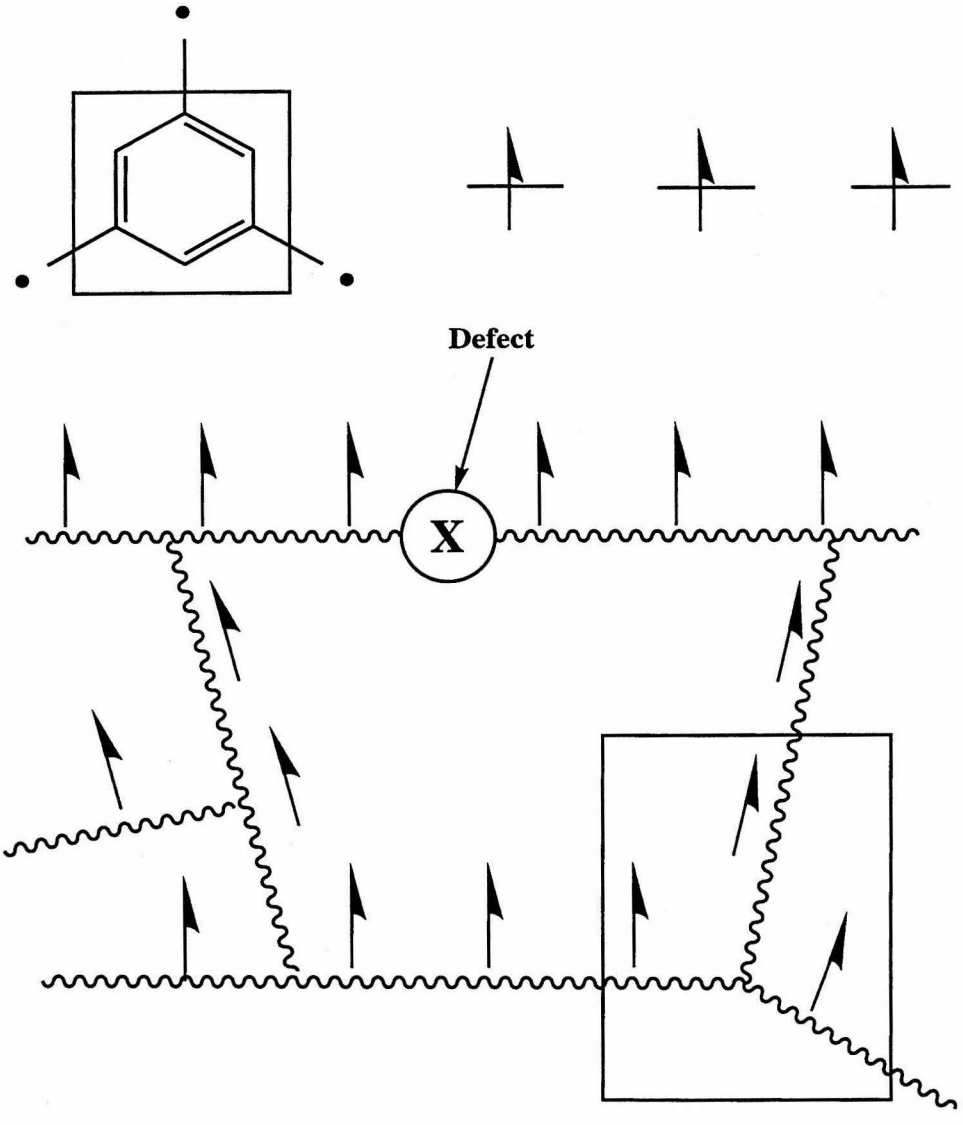
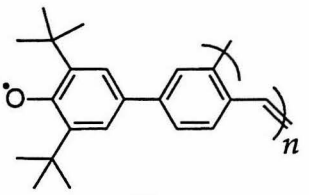



**Figure 2-23.** Overcoming defects by cross-linking of polymer chains.

An alternative solution to defect formation employing a *conducting* topology has recently been advanced by Nishide.[102] It is proposed that long-range ferromagnetic spin alignment of radicals at either side of a defect in **50**

is possible through the π-conjugated backbone. Such a strategy is attractive as pristine polymer would retain full solubility, but a careful choice is SC must be made to ensure adequate spin delocalization into the conjugated polymer chain.



**50**

**Experimental Section**

**$AsF_5$ Doping Procedure**

A known mass of polymer (film or powder) is placed in a dry vial. The vial is then placed in an oven-dried doping chamber in a nitrogen-filled glovebox. O-rings were coated with Halocarbon™ —a chlorofluorocarbon-based grease resistant to oxidation, and available from Halocarbon Corporation, Hackensack, New Jersey. The polymer sample and a 100 ml cold finger were pumped down overnight on a purpose-built vacuum line fitted with an MKS Instruments AA01000A pressure transducer and a PdRC-1B readout/power supply unit. The vacuum line was thoroughly dried with heat guns under dynamic vacuum before the introduction of any $AsF_5$. Both the polymer sample and cold finger were then isolated from the line by closing their respective Teflon valves. These experiments were conducted under static vacuum; the vacuum pump was isolated from the line, the pressure transducer zeroed using a small screwdriver and $AsF_5$ slowly introduced by opening a large valve on the cylinder itself and a smaller valve attached to it via a metal joint. The doping chamber was then opened to the vacuum line and pressure allowed to rise to the desired value. It was found useful to pump a little $AsF_5$ into the metal joint between the two valves. The smaller valve may then be opened to allow a continuous small amount of $AsF_5$ into the doping chamber. This procedure enables the experimenter to compensate for dopant uptake by polymers and is especially useful for lightly doped samples. Once doping has proceeded for the desired time, all valves are closed to $AsF_5$ and the cold finger is immersed in liquid nitrogen and opened to the vacuum line. Excess dopant is condensed into the finger and the pressure falls close to zero. It may quenched by adding acetone while still cold. White fumes are produced in the process. The entire system is then

subjected to dynamic vacuum and pumped down overnight. The doping chamber is then brought into the glovebox and the sample vial reweighed to determine dopant uptake. Polymer samples typically turn brown, blue and finally black when exposed to this oxidant. Lightly doped polymer films retain their flexibility whereas heavily doped samples are brittle.

**Solution Phase Doping Procedures**

A polymer sample (20-50 mg) is placed in a tared vial fitted with a magnetic stirbar in the glovebox. A minimal amount (3-5 ml) of methylene chloride or tetrahydrofuran is added to the sample, together with the desired dopant. Iodine was added in approximately 50% excess as the counterion is expected to be $I_3^-$. Other oxidants such as silver perchlorate, silver tetrafluoroborate and nitrosonium tetrafluoroborate were added in stoichiometric amounts. The mixture was stirred in the glovebox for a fixed period of time and then fitted with a rubber septum and removed from the box. Dry argon was then blown over the sample to remove solvent. The vial is then reintroduced into the glovebox, placed into a 24/40 round-bottomed flask fitted with a gas inlet adapter and pumped down under high vacuum overnight. Subsequent weighing allows an estimation of dopant uptake (only relevant for iodine-doped samples).

**Materials**

Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl. Toluene, methylene chloride, and trimethylsilyl chloride were distilled from $CaH_2$. 2,5-dibromothiophene (**34**) was redistilled before use. All other starting materials were used as received.

**Instrumentation**

NMR spectra were recorded on a JEOL-GX 400 (399.65 MHz $^{1}H$, 100.4 MHz $^{13}C$) or a GE-300 spectrometer in $CDCl_3$ at room temperature and referenced to residual protons unless specified otherwise. IR spectra were measured on a Perkin-Elmer 1600 instrument in a KBr pellet unless specified otherwise. Melting points were recorded on a Thomas Hoover melting point apparatus and are uncorrected. EI mass spectra , 70 eV, were obtained on a Hewlett-Packard 5890/5970 GC/MS. FAB and exact mass measurements were performed on a ZAB 7070 instrument at the University of California, Riverside. UV/visible spectra were recorded on a Beckman Instruments DU-640 continuous wave spectrometer. Elemental analysis was determined at Atlantic Microlab, Norcross, Georgia and Galbraith Laboratories, Knoxville, Tennesse. Gel permeation chromatography was performed on a homemade instrument employing either 3 Shodex size Styragel columns, (KF 803, KF 804, and KF 805) or an American Polymer Standards 10-μm mixed-bed column, an Altex model 110A pump, a Knauer differential refractometer and a Kratos UV detector. Methylene chloride was used as an eluant at a flow rate of 1 mL/min. Molecular weights are reported relative to narrow polystyrene standards, polymer solutions (0.5% w/v) were passed through a 0.5 μm filter before injection.

**Magnetization Studies**

Variable field and temperature measurements were performed on a Quantum Design MPMS Squid Magnetometer. Samples were held in delrin screw-cap holders and loaded in the glovebox. Polymer samples were handled with Teflon-coated or plastic tweezers to avoid contamination by transition metals. The diamagnetic correction of the sample and holder, $\chi_{dia}$,

was determined from a plot of magnetic susceptibility, $\chi_e$, versus inverse temperature. The correction may be estimated from the intercept upon extrapolation to infinite temperature. The plot was linear between 50 and 180 K. The magnetization of the sample was measured between 0 and 55 kG at constant temperature, (1.8 or 4.5 K), starting with the high field measurement to ensure saturation of ferromagnetic impurities throughout the curve. The spin state of the material, $S$, was determined from a two-parameter Brillouin fit that simultaneously evaluates both $S$ and the paramagnetic saturation moment $M_{sat}$. Variable temperature behavior was determined between 2 and 300 K at constant field (usually 1 kG).

The spin concentration was evaluated most conveniently from the variable field plot as follows: the experimentally determined saturation moment expressed in emuG/g is converted to molar quantities by multiplying by the effective molecular weight, $M^r$, of the doped polymer's repeat unit. The molecular weight is compensated for dopant uptake:

$$M_{sat}\,(\text{emu}\bullet\text{G/mol}) = M_{sat}\,(\text{emu}\bullet\text{G/g}) \times M^r(\text{g/mol}). \qquad (9)$$

The saturation moment expected for a mole of molecules of spin, $S$, is described by:

$$M_{sat}\,(\text{emu}\bullet\text{G/mol}) = Ng\mu_\beta S, \qquad (10)$$

where $N$ is Avogadro's number, g is the Landé splitting factor and $\mu_b$ is the Bohr magneton. Assuming g = 2, this can be written as:

$$M_{sat}\,(\text{emu}\bullet\text{G/mol}) = 1.117\text{x}10^4 S. \qquad (11)$$

$$\text{Thus for } S = {}^1/_2\text{: \% monomers doped} = \frac{M_{sat}\ (\text{emuG/mol})}{1.117 \times 10^4 \text{x}\ 0.5} \times 100 \qquad (12)$$

**Synthesis**

**Poly[(5-Octadecyloxymetaphenylene) vinylene thienylene vinylene] (1).** Bisphosphonium salt **20** (3.5237 g, 3.3336 mmol) was added to a 100 ml Schlenk flask fitted with a magnetic stirbar. Toluene (20 ml) was added and the mixture stirred at room temperature for 20 min before 2.85 ml (6.67 mmol) of a 2.33 M *n*-BuLi solution in hexanes was added via syringe. The red opaque mixture was heated to reflux for 35 min. Dialdehyde **21** (0.4675 g, 3.334 mmol) dissolved in 20 ml of toluene was added via a teflon cannula. The solution turned orange towards the end of the addition. The mixture was then refluxed under argon for 72 h. The solvent was then removed and the residue extracted with methanol for 72 h yielding 1.2626 g (79%) of yellow polymer. $^1$H NMR δ 0.86 (br, 3 H), 1.23 (br, 30 H), 1.75 (br, 2 H), 3.9 (br, 2 H), 6.5-7.4 (br, 9 H); IR (NaCl) 3016, 2922, 2851, 1582, 1465, 1299, 1167, 1057, 944, 850, 823 cm$^{-1}$; GPC $M_n$ = 7040, $M_w$ = 14500, PDI = 2.06, (MW of monomer = 479); UV($CHCl_3$) $\lambda_{max}$ = 410 nm additional peak at 436 nm. Anal. Calcd for $C_{32}H_{46}OS$: C, 80.28; H, 9.68; O, 3.34; S, 6.70. Found: C, 79.93; H, 9.91; O, 3.95; S, 6.76, P < 0.45; Br, < 0.5.

**Poly[(5-Octadecyloxy-meta-phenylene) vinylene bithienylene vinylene] (2).** Bisphosphonium salt **20** (1.5115 g, 1.4300 mmol), bisaldehyde **22** (0.3179 g, 1.430 mmol) and 20 ml of toluene were combined in a 50 ml Schlenk flask fitted with a stirbar. The mixture was stirred for 5 min. A solution of potassium *t*-butoxide in THF (1.0 M, 4.4 ml) was then added dropwise and the mixture went deep red in color. The solution was slowly warmed and refluxed under argon for 4 days. The brown mixture was then cooled and added to methanol (100 ml) yielding a brown solid. Soxhlet extraction with methanol yielded 420 mg (52%) of yellow-brown polymer. $^1$H NMR δ 0.86 (br, 3 H), 1.23 (br, 30 H), 1.79 (br, 2 H), 3.9 (br, 2 H), 6.5-7.4 (br, 11 H); IR 3063, 3020,

2921, 2850, 1618, 1582, 1465, 1434, 1295, 1167, 1056, 943, 815, 786, 721, 678 $cm^{-1}$ ; GPC $M_n$ = 9730, $M_w$ = 12710, PDI = 1.31, (MW of monomer = 561); UV($CHCl_3$) $\lambda_{max}$ = 432 nm, additional peak at 266 nm. Anal. Calcd for $C_{36}H_{48}OS_2$: C, 77.09; H, 8.73; O, 2.84; S, 11.43. Found: C, 77.16; H, 8.52; O, 3.17; S, 10.11, P < 0.4; Br, < 0.05.

**5-Hydoxydimethylisophthalate, (16).** 5-hydroxy-isophthalic acid (23.00 g, 0.1263 mol), methanol (1250 ml) and sulfuric acid (3 ml) were refluxed together for eight hours. The mixture was then cooled and the solvent evaporated. Crude product was redissolved in diethyl ether, washed with water and dried over $MgSO_4$ to yield 14.96 g (56%) of desired product.

$^1$NMR (acetone-$d_6$) δ 2.89 (bs, 1 H); 3.90 (s, 6 H); 7.67 (d, J = 1.5 Hz, 2 H); 8.10 (t, J = 1.5 Hz, 1 H).

**5-Octadecyloxydimethylisophthalate, (17).** To a three-necked 2 L flask fitted with a magnetic stirrer was added **16**, (22.22g, 0.1057 mol) and reagent grade acetonitrile (1.2 L). Potassium carbonate (155.51g, 1.1252 mol) was added and the white heterogeneous mixture was heated to reflux. Octadecyl bromide (35.45g, 0.1063 mol) was added and reflux was continued for 20 hours. The white reaction mixture was then hot gravity-filtered and the solvent evaporated. Crude brown product was recrystallized from petroleum ether to yield 31.79 g (65%) of pure **17** as a white solid. $^1$H NMR δ 0.87 (t, J = 6.8 Hz, 6.24 Hz, 3 H, ); 1.24 ( bs, 30 H ); 1.43 (bs, 2 H ); 3.92(s, 6 H); 4.02 (t, J = 6.4 Hz, 2 H); 7.73 (s, 2 H); 8.24 (s, 1 H). $^{13}$C NMR δ 14.21 ; 22.77 ; 26.05; 29.17; 29.44; 29.65; 29.67; 29.78; 32.01; 52.45; 68.66;119.86; 122.78; 131.71; 159.28; 166.27.

**5-Octadecyloxy-1,3- benzenedimethanol, (18).** Anhydrous THF (750 ml), $LiAlH_4$ (3.67 g, 0.0967 mol) and diester **17** (20.40 g, 0.0441 mol) were refluxed together under argon for four hours with mechanical stirring and cooled to room temperature. Excess $LiAlH_4$ was quenched by the slow addition of

water and the mixture filtered. Solvent was removed under vacuum and the resulting solid redissolved in diethyl ether, washed with water, dried over $MgSO_4$ and concentrated to yield 10.36 g (58%) of pure diol. $^1H$ NMR δ 0.86 (t, 3 H); 1.25 (bs, 30 H); 1.43 (bs, 2 H); 1.65 (m, 2 H); 3.96 (t, J = 6.5 Hz, 2 H); 4.65 (s, 4 H); 6.83 (s, 1 H); 6.91 (s, 1 H). $^{13}C$ NMR δ 14.09; 22.68; 26.07; 29.30; 29.36; 29.70; 31.93; 65.27; 68.13; 112.24; 117.30; 142.77; 159.79.

**1,3-Bis(bromomethyl)-5-octadecyloxybenzene (19).** A slow stream of hydrogen bromide was passed overnight through a stirred suspension of diol **18** (5.00 g, 12.3 mmol) in benzene (50 ml). The resulting clear colorless solution was filtered through a silica gel plug and the filtrate was evaporated to yield 5.35 g (82% yield) of white dibromide **19**. Recrystallization (hexanes) gave 4.70 g (72% yield) of white solid: mp 71-72 °C; $^1H$ NMR δ 0.88 (t, J = 6.8 Hz, 3 H), 1.25 (br, 28 H), 1.44-1.52 (m, 2 H), 1.75-1.80 (m, 2 H), 3.95 (t, J = 6.5 Hz, 2 H), 4.43 (s, 4 H), 6.85 (s, 2 H), 6.98 (s, 1 H); $^{13}C$ NMR δ 14.10, 22.67, 26.00, 29.17, 29.35, 29.55, 29.58, 29.65, 29.68, 31.91, 32.88, 68.18, 115.18, 121.54, 139.50, 159.56; IR 2918, 1850, 1328, 698 $cm^{-1}$; EIMS, m/z 534(50), 533(27), 532(100), 530(50), 201(31), 199(30). Anal. Calcd for $C_{26}H_{44}Br_2O$: C, 58.65; H, 8.33; Br, 30.02. Found: C, 58.70; H, 8.33; Br, 29.90.

**5-Octadecyloxybenzene-1,3-bis(methyltriphenylphosphonium) bromide (20).** Triphenylphosphine (4.04 g, 15.4 mmol) and dibromide **19** (3.73 g, 6.98 mmol) were refluxed in dry acetonitrile (30 ml) under an atmosphere of dry argon overnight. The solvent was evaporated, white residue was vacuum dried, dissolved in chloroform and precipitated from ether hexane mixture (5:1). The precipitation process was repeated twice, and the product was vacuum dried (12 hr, 120 °C) to yield a white solid: mp 141-143 °C; $^1H$ NMR δ 0.87 (t, J = 6.5 Hz, 3 H), 1.17-1.40 (m, with maximum at 1.27, 32 H), 3.33 (t, J = 5.9 Hz, 2 H), 5.15 (d, J = 14.4 Hz, 4 H), 6.51 (s, 2 H), 7.05 (br s, 1 H), 7.61-7.66 (m, 12

H), 7.71-7.76 (m, 18 H); $^{13}C$ NMR δ 13.78, 22.32, 25.57, 28.49, 28.99, 29.03, 29.26, 29.30, 29.35 (3C), 29.38 (3C), 29.86, 31.56, 67.72, 117.22 (d, J = 86 Hz), 117.44, 126.16 (br), 129.01 (d, J = 11 Hz), 129.91 (d, J = 12.5 Hz), 134.15 (d, J = 10.3 Hz), 134.62, 158.43 (br); $^{31}P$ NMR δ 26.21 (s); FAB MS, m/z 977 and 975(M-Br, 7), 896(73), 895(100), 634(21), 262(32), 183(42). Anal. Calcd. for $C_{62}H_{74}P_2Br_2O$: C, 70.45; H, 7.06; O, 1.51; P, 5.86; Br, 15.12. Found: C, 70.79; H, 7.06; O, 0.90; P, 5.97; Br, 15.16.

**Poly[(5-tetradecyl-meta-phenylene) thienylene] (2).** 2,5-Dibromothiophene (**34**, 0.5402 g, 2.233 mmol), bisboronic ester **33** (1.1121 g, 2.1794 mmol) and $Pd(PPh_3)_4$ (30 mg) were combined in a 50 ml Schlenk flask in the glove box. Toluene (20 ml) was added and the solution purged with argon. A deoxygenated, aqueous $Na_2CO_3$ (2 M, 5 ml) solution was then added and the heterogeneous mixture slowly brought to reflux under argon. The resulting yellow solution was refluxed for 72 hr, cooled and added to acetone (150 ml). The resulting filtrate was washed with 1% v/v HCl solution, extracted with hot toluene and precipitated with acetone yielding 348 mg (45%) of yellow polymer. $^1H$ NMR ($CD_2Cl_2$) δ 0.86 (br, 3 H), 1.23 (br, 22 H), 1.66 (br, 2 H), 2.65 (br, 2 H), 7.1-7.5 (br, 4 H), 7.5-7.8 (br, 1 H); IR 3071, 2851, 1592, 1466, 1376, 1238, 1095, 994, 862, 796, 721, 691 $cm^{-1}$ ; GPC: $M_n$ = 9510, $M_w$ = 11720, PDI = 1.23, (MW of monomer = 355); UV($CHCl_3$) $\lambda_{max}$ = 345 nm. Anal Calcd for $C_{24}H_{34}S$: C, 81.30; H, 9.66; S, 9.04. Found: C, 80.56; H, 9.12; S, 8.39.

**Poly[(5-tetradecyl-meta-phenylene) 2,2'-bithienylene] (3).** Dibromide **35** (0.5131 g, 1.651 mmol), bisboronic ester **33** (823.0 mg, 1.613 mmol) and $Pd(PPh_3)_4$ (22.9 mg) were added to a 50 ml Schlenk flask. Toluene (20 ml) and a solution of $Na_2CO_3$ (2 M, 4 ml) were added and the pale yellow heterogeneous mixture purged with argon and warmed slowly to reflux temperature. The yellow solution was refluxed under argon for 72 h, allowed to cool to room temperature and added to 150 ml of acetone. The resulting

yellow precipitate was washed with warm water, extracted with ethanol and 1,1,1-trichloroethane. The high molecular weight fraction was extracted with xylenes and reprecipitated with methanol to yield 499 mg (71%) of yellow polymer. $^1$H NMR ($CDCl_3$, 50 °C) δ 0.86 (br, 3 H), 1.25 (br, 22 H), 1.70 (br, 2 H), 2.66 (br, 2 H), 7.1-7.5 (br, 6 H), 7.6-7.7 (br, 1 H); IR 3068, 2921, 2849, 1588, 1452, 1364, 1235, 864, 791 $cm^{-1}$; GPC $M_n$ = 7040, $M_w$ = 7820, PDI = 1.11, (MW of monomer = 437); UV($CHCl_3$) $\lambda_{max}$ = 390 nm. Anal. Calcd. for $C_{28}H_{36}S_2$: C, 77.01; H, 8.31; S, 14.68. Found: C, 77.81; H, 8.37; S, 14.76.

**2,6-Dibromo-4-tetradecylaniline (30).** 4-Tetradecylaniline (25.0 g, 86.4 mmol) was dissolved in acetic acid (250 ml) and bromine (28.0 g, 173 mmol) was slowly added at room temperature. The white thick suspension was stirred overnight, poured into water, and the precipitate was filtered off. The crude product was recrystallized from *i*-propanol to yield 35.4 g (91% yield) of pale crystals: mp 78-80 °C; $^1$H NMR δ 0.88 (t, J = 6.5 Hz, 3 H), 1.25 (br, 22 H), 1.50-1.56 (m, 2 H), 2.44 (t, J = 7.5 Hz, 2 H), 4.38 (br s, 2 H), 7.19 (s, 2 H); $^{13}$C NMR δ 14.12, 22.69, 29.08, 29.35, 29.42, 29.54, 29.65 (2C), 29.68 (2C), 31.40, 31.92, 34.41, 108.72, 131.53, 134.61, 139.63; IR 3432, 3342, 2952, 2918, 2846, 1617, 1577, 1543, 1468, 864, 732, 712 $cm^{-1}$; EIMS, m/z 449(53), 447(100), 445(50), 266(33), 264(69), 262(34). Anal. Calcd for $C_{20}H_{33}Br_2N$: C, 53.70; H, 7.44; Br, 35.73; N, 3.13. Found: C, 53.75; H, 7.44; Br, 35.65; N, 3.14.

**1,3-Dibromo-5-tetradecylbenzene (31).** The dibromoaniline **30** (35.0 g, 78.3 mmol) was slowly (45 min) added to a stirred warm mixture of DMF (55 °C, 350 ml) and *t*-butyl nitrite (90%, 20 g) under a blanket of argon. The resulting brown-yellow solution was stirred for 30 min, cooled down and poured into 1% hydrochloric acid. The product was extracted twice with hexanes, the organic phase was dried and filtered through a silica gel plug. The almost colorless filtrate was evaporated and the resulting residue was Kugel-rohr

distilled (210 °C/0.2 Torr). The yellowish distillate was dissolved in pentane, filtered through silica gel and the filtrate evaporated to yield 23.62 g of 90% pure (by GC) dibromide. Analytical sample was obtained by recrystallization of the crude product from ethanol-hexane: mp 38 °C; $^{1}$H NMR δ 0.88 (t, J = 6.5 Hz, 3 H), 1.25 (br, 22 H), 1.53-1.59 (m, 2 H), 2.53 (t, J = 7.5 Hz, 2 H), 7.25 (d, J = 1.7 Hz, 2 H); 7.47 (t, J = 1.7 Hz, 1 H); $^{13}$C NMR δ 14.12, 22.69, 29.12, 29.36, 29.38, 29.50, 29.62, 29.65 (2C), 29.68, 29.69, 31.01, 31.92, 35.37, 122.66, 130.26, 131.27, 146.88; IR 2925, 2853, 1585, 1553, 1420, 849, 741 cm$^{-1}$; EIMS, m/z 434(32), 432(62), 430(31), 252(51), 250(100), 248(53). Anal. Calcd for $C_{20}H_{32}Br_2$: C, 55.57; H, 7.46; Br, 36.97. Found: C, 55.54; H, 7.43; N, 37.08.

**1,3-Bis(trimethylsilyl)-5-tetradecylbenzene (32).** Mg turnings (2.601 g, 0.111 mol), THF (15 ml), and trimethylsilyl chloride (13.696 g, 0.1261 mol) were stirred in a 250 ml, three-necked flask fitted with a reflux condenser and an addition funnel. The Grignard reaction was activated by the addition of a few drops of dibromoethane and dibromide **31** (21.30 g, 0.0493 mol) dissolved in 50 ml of THF was slowly added over a 1 h period. The resulting red solution was refluxed under argon for 18 hours. The mixture was then cooled, added to hexane (150 ml) and washed with saturated $NH_4Cl$ solution (100 ml). The aqueous layer was further extracted with 2 x 50 ml of hexane and the combined organic extracts passed through 2 in of silica gel. Concentration yielded 11.47 g of crude (79% pure by GC/MS) product. The sample may be further purified (> 95%) by vacuum distillation (bp = 170 °C/ 55 mtorr). $^{1}$H NMR δ 0.27 (s, 18 H), 0.86 (t, J = 6.8 Hz, 3 H); 1.25 (br, 22 H), 1.61 (br m, 2 H), 2.60 (t, J = 7.8 Hz, 2 H), 7.33 (s, 2 H), 7.49 (s, 1 H) ; $^{13}$C NMR δ -0.99, 14.16, 22.74, 29.42, 29.57, 29.61, 29.70, 29.74, 31.88, 31.98, 36.33, 134.06, 135.50, 139.25, 141.12; EIMS, m/z 418(M, 11), 404(38), 403(M-15, 100), 329(12), 221(9), 73(95).

**5-Tetradecylbenzene-1,3-bis-(1,3,2-benzodioxaborole) (33).** Crude 1,3-

Bis(trimethylsilyl)-5-tetradecylbenzene **32** (803 mg, 1.92 mmol) was dissolved in methylene chloride (10 ml) and the solution cooled to –78 °C. A solution of $BBr_3$ in methylene chloride (1.0 M, 3.8 ml) was slowly added with stirring. The resulting pale yellow suspension was then allowed to slowly warm to room temperature and refluxed for 24 hours under argon. The red solution was cooled in an ice-bath and catechol (0.423 g, 3.84 mmol) was added in one portion. The white suspension was stirred at room temperature for 24 hours and filtered. The filtrate was redissolved in methylene chloride and passed through a short column of neutral alumina. Recrystallization from chloroform afforded 496 mg (50.7%) of pure bisboronic ester. mp 144-145 °C; $^1$H NMR δ 0.87 (t, J = 6.8 Hz, 3 H), 1.25 (br, 22 H), 1.71 (br m, 2 H), 2.75 (t, J = 7.8 Hz, 2 H), 7.15 (dd, J = 3.4, 2.4 Hz, 4 H), 7.35 (dd, J = 3.4, 2.4 Hz, 4 H), 8.10 (s, 2 H), 8.66 (s, 1 H) ; $^{13}$C NMR (50 °C) δ 14.02, 22.68, 29.36, 29.40, 29.53, 29.62, 29.69, 31.50, 31.95, 35.95, 112.61, 122.83, 125.88 (br, C-B), 138.86, 139.36, 142.62, 148.71; IR 3033, 2918, 2872, 1600, 1473, 1454, 1397, 1303, 1235, 1136, 914, 863, 811, 741, 706 $cm^{-1}$; FAB, m/z 510(M, 4), 327(12), 235(8), 209(11), 137(13), 136(100), 121(10), 120(21); HRMS 510.3105, calcd. for $C_{32}H_{40}B_2O_4$ 510.3113 ; Anal Calcd for $C_{32}H_{40}B_2O_4$: C, 75.32; H, 7.90; B, 4.24. Found: C, 75.35; H, 7.96; B, 4.16

**5,5'-Dibromo-2,2'-Bithiophene (35).**[103] 2,2'-Bithiophene (1.171 g, 7.04 mmol) was placed in a 100 ml three-necked flask fitted with a magnetic stirbar. Glacial acetic acid (50 ml) was added and the clear solution stirred briefly. *N*-Bromosuccinimide (2.512 g, 14.11 mmol) was added portionwise and the mixture stirred for ten minutes whereupon a white precipitate formed. Additional glacial acetic acid (30 ml) was added and stirring continued for 20 hours. The mixture was then added to a mixture of water (100 ml) and chloroform (200 ml). The layers were separated and the aqueous layer extracted with additional chloroform (2 x 75 ml). Combined organic

extracts were washed with water, dried over $CaSO_4$ and concentrated. Recrystallization from heptane furnished 1.769 g (78%) of pure dibromide as pale plates. mp 143°C; $^1$H NMR δ 6.85 (d, J = 3.8 Hz, 2 H); 6.96 (d, 3.8 Hz, 2 H); EIMS , m/z 324(M, 100); 326(58); 322(48); 245(15); 201(15); 164(16); Anal Calcd for $C_8H_4S_2Br_2$: C, 29.83; H, 1.25; S: 19.87; Br: 49.05. Found: C, 28.77; H, 1.26; S, 19.80; Br, 48.93.

**2,5-Bischloromethyl-thiophene (23).** To a clean, dry 250 ml three-necked flask fitted with a magnetic stirbar and thermometer was added an aqueous formaldehyde solution (100 ml, 37%, 1.375 mol) and concentrated hydrochloric acid (37%, 25 ml). Hydrogen chloride was passed through the solution for approximately forty five minutes maintaining the temperature below 75°C. The reaction mixture was cooled to 30°C before thiophene (34.68 g, 0.4122 mol) was added dropwise via an addition funnel. The reaction mixture turned dark brown in color and the temperature was maintained below 50°C during the addition. Stirring was continued for a further twenty five minutes and the black organic layer separated and washed with 5 x 25 ml of cold water. The brown liquid was collected and refrigerated overnight to yield 60.02 g (80%) of crude product. An analytical sample was obtained by scratching the flask to promote crystallization. mp 32-34°C; $^1$H NMR δ 7.26 (s, 3 H); 4.59 (s, 6 H); EIMS, m/z 182(M, $^{37}$Cl, 17); 180(M, $^{35}$Cl, 23); 145(100); 110(58).

**1,1'-(2,5-Thiophenediyldimethylene) bis [pyridinium chloride] (24).**[47] Bischloride **23** (4.74 g, 0.026 mol), pyridine (5.3 g, 0.067 mol) and absolute ethanol, (5 ml) were warmed together on a heating bath for thirty minutes. The resulting white precipitate was collected and recrystallized from absolute ethanol to yield 5.69 g (65%) of desired product as a hygroscopic white solid. $^1$H NMR ($CD_3OD$) δ 6.11 (s, 4 H); 7.47 (s, 2 H); 8.14 (m, 4 H); 8.63 (t, J = 7. 8 Hz, 2 H); 9.12 (d, J = 5.6 Hz, 4 H).

**α-α'-(2,5-Thiophenediyl) bis [*N*-(*p*-dimethylaminophenyl)-nitrone] (25).**[47] Bispyridinium salt **24** (49.94 g, 0.145 mol) and ethanol (600 ml) were combined in a 1 L Erlenmeyer flask. *p*-Nitroso *N, N*-Dimethylaniline (38.8 g, 0.258 mol) was added under ice cooling. Sodium hydroxide (10.9 g, 0.273 mol) dissolved in water (270 ml) was slowly added with stirring. The resulting dark brown mixture was stirred for one hour at 0°C and for a further two hours at room temperature. Water (500 ml) was then added and the mixture allowed to stand overnight. The dark brown precipitate was collected and recrystallized to yield **25** as sparingly soluble small red crystals. Yield = 67%; mp 256-258°C.

**2,5-Thiophenedicarbaldehyde (21).**[47] Bisnitrone **25** (13.00 g, 0.0318 mol) was slowly added to an ice-cooled mixture of concentrated hydrochloric acid (95 ml) in distilled water (185 ml). The brown-red solution was stirred for thirty five minutes under ice-cooling and extracted with diethyl ether (1 x 150 ml) and (8 x 50 ml). The combined organic layers were dried over $MgSO_4$ and concentrated to yield a brown solid. Column chromatography on silica gel (methylene chloride as eluant) followed by recrystallization from ethanol afforded 1. 64 g (37%) of desired product. mp 114.5-115.5 °C. $^1$H NMR δ 7.84 (s, 2 H), 10.04 (s, 2 H); $^{13}$C NMR δ 134.83, 149.24, 183.25. Anal. Calcd for $C_6H_4SO_2$: C, 51.42; H, 2.88. Found: C, 51.22; H, 2.94.

**2,2'-Bithiophene-5,5'-dicarbaldehyde (22).**[49] 2,2'-bithiophene (1.124 g, 6.760 mmol) was dissolved in diethyl ether (35 ml) and the solution cooled to –5 °C. A solution of *n*-BuLi in hexanes (2.5 M, 5.5 ml) was added dropwise via a syringe. The cloudy mixture was slowly allowed to rise to room temperature and refluxed under argon for 90 minutes. Anhydrous DMF (1.134 g, 15.51 mmol) dissolved in THF (35 ml) was then added at 0 °C and the reactants stirred at room temperature overnight, added to HCl (10 %, 200 ml) and neutralized with sodium bicarbonate. Filtration yielded a crude brown solid

which was recrystallized from chloroform (twice) and sublimed at 170 °C/20 mtorr. Yield = 776 mg (52%). mp 213-214 °C lit., mp 215-216.5 °C; $^1$H NMR δ 7.40 (d, J = 4.0 Hz, 2 H), 7.71 (d, J = 4.0 Hz, 2 H), 9.90 (s, 2 H); $^{13}$C NMR δ 126.47, 136.89, 143.86, 144.82, 182.53; Anal. Calcd. for $C_{10}H_6S_2O_2$: C, 54.04; H, 2.72; S, 28.85. Found: C, 54.03; H, 2.70; S, 28.75.

**Alkoxythiophene (38).** To a solution of 3-bromothiophene (15.66 g, 0.0961 mol) and triethyleneglycol monomethyl ether (23.60 g, 0.1437 mol) in dry pyridine (100 ml) was added potassium *t*-butoxide (17.64 g, 0.1572 mol) and copper (I) iodide (3.64 g, 0.0191 mol). The reaction mixture went deep red in color, was refluxed under argon overnight, cooled to room temperature and filtered. The filter cake was washed well with methylene chloride. Pyridine was removed under vacuum and the residue was redissolved in methylene chloride. The two solutions were combined, washed well with 15% HCl (200 ml), then brine and the organic layer was dried over $MgSO_4$ and concentrated yielding a black residue. Subsequent distillation at 164°C/110 mtorr afforded 16.185 g,( 68.4%) of pure **38**. $^1$H NMR δ 3.35 (s, 3 H); 3.40-3.83 (m, 10 H); 4.09 (t, J = 4.7 Hz, 2 H); 6.23 (m, 1 H); 6.75 (dd, J = 5.2, 3.1 Hz, 1 H); 7.14 (dd, J = 5.2, 3.1 Hz, 1 H); $^{13}$C NMR δ = 58.87; 69.40; 69.52; 70.40; 70.48; 70.61; 71.76; 97.32; 119.43; 124.47; 157.42; Exact Mass (FAB): Calculated: 246.0926; Found: 246.0937 (+4.4 ppm).

**Bisalkoxy Bithiophene (39).** To a solution of **38** (7.153 g, 0.2761 mol) in anhydrous THF (20 ml) cooled to 0°C was added *n*-BuLi (2.5 M, 12.5 ml, 0.0312 mol) portionwise over a five minute period. The red solution was stirred at 0°C for thirty minutes and transferred via cannula to a solution of $Fe(acac)_3$ (9.64 g, 0.0273 mol) in dry THF (150 ml). The reaction mixture was brought to reflux under argon and gradually formed a dark precipitate. Reflux was continued for eight hours, cooled and stirred at room temperature overnight.

The mixture was then filtered and the filter cake washed with additional THF. Concentration of the filtrate yielded a red oil which was redissolved in diethyl ether (200 ml), washed with water and dried over $MgSO_4$. Chromatography on silica gel using ethyl acetate as eluant furnished 4.462 g (65.9%) of **39** as a yellow solid. mp 45-46°C; $^1$H NMR δ 3.37 (s, 6 H); 3.54 (m, 4 H); 3.68 (m, 8 H); 3.76 (m, 4 H); 3.90 (t, J = 5.0 Hz, 4 H); 4.25 (t, J = 5.0 Hz, 4 H); 6.85 (d, J = 4.6 Hz, 2 H); 7.07 (d, J = 4.6 Hz, 2 H); $^{13}$C NMR δ 58.96; 69.95; 70.49; 70.66; 70.85; 71.30; 71.86; 114.67; 116.49; 121.82; 151.63; Exact Mass (FAB): Calculated: 490.1695; Found: 490.1688 (-1.4 ppm).

**1,3-Dithienyl-5-Tetradecylbenzene (40).** 2-Tributylstannyl thiophene (3.76 g, 10.1 mmol), dibromide **31** (1.997 g, 4.62 mmol)and dry THF (35 ml) were combined in a 100 ml three-necked flask. The solution was purged with argon and $Pd(PPh_3)_2Cl_2$ (100 mg, 3%) was added and the pale yellow solution was brought to reflux overnight. The solution's color slowly darkened and turned black after 24 hours and still contained starting material as detected by tlc. The reaction mixture was refluxed for a further 24 hours, cooled to room temperature and concentrated. Column chromatography on silica gel (3% $CHCl_3$/hexanes) followed by recrystallization from hexanes/ethanol afforded 1.802 g (89%) of pure product. mp 50-51°C; $^1$H NMR δ 0.88 (t, J = 6.6 Hz, 3 H); 1.25 (bs, 22 H); 1.67 (m, 2 H); 2.66 (t, J = 7.7 Hz, 2 H); 7.10 (m, 2 H); 7.30 (m, 2 H); 7.36 (m, 4 H); 7.66 (s, 1 H); $^{13}$C NMR δ 14.11; 22.69; 29.35; 29.51; 29.60; 29.67; 31.42; 31.93; 35.94; 121.17; 123.32; 124.85; 125.37; 127.93; 134.93; 144.24; 144.27; Exact Mass (FAB): Calculated: 438.2415; Found: 438.2418 (+0.8 ppm).

**Dibromide 41.** To 50 ml of a 1:1 mixture of glacial acetic acid/chloroform was added **39** (883 mg, 2.01 mmol) and *N*-bromosuccinimide (779 mg, 4.38 mmol). The mixture was stirred overnight at room temperature. The reaction's progress was monitored by $^1$H NMR and showed significant

amounts of monobrominated product. A further equivalent of *N*-bromosuccinimide (340 mg, 2.19 mmol) was added and the mixture was allowed to stir for another 12 hours and concentrated. The white residue was redissolved in methylene chloride, washed with water and the organic extract was passed through a short column of silica gel. Recrystallization from hexanes/ethanol afforded 1.020 g (85%) of pure dibromide as white needles. mp 76-77°C; $^{1}$H NMR δ 0.89 (t, J = 6.5 Hz, 3 H); 1.27 (bs, 22 H); 1.68 (m, 2 H); 2.65 (t, J = 7.7 Hz, 2 H); 7.04-7.09 (m, 4 H); 7.25-7.27 (m, 2 H); 7.45 (s, 1 H); $^{13}$C NMR δ 14.11; 22.70; 29.29; 29.36; 29.47; 29.57; 29.67; 31.33; 31.93; 35.86; 111.66; 120.38; 123.60; 125.35; 130.83; 134.36; 144.69; 145.41; Exact Mass (FAB): Calculated: 596.0605; Found: 596.0589 (-2.7 ppm).

**1,3-Bisoctadecyloxybenzene (42).** Resorcinol (4.00 g, 0.0363 mol), 1-octadecylbromide (24.52 g, 0.0735 mol) and reagent grade acetonitrile (150 ml) were combined in a flask fitted with a mechanical stirrer. Potassium carbonate (30.18 g, 0.2184 mol) was added and the mixture brought to reflux for fifteen hours. Additional potassium carbonate (3.25 g, 0.0235 mol) and octadecylbromide (3.17 g, 9.51 mmol) were added and reflux continued for a further five hours. The reaction mixture was filtered while hot and the filter cake washed well with warm chloroform. Concentration of the mother liquor affords 10.53 g (47%) of pure product. mp 77-78°C; $^{1}$H NMR δ 0.88 (t, J = 6.5 Hz, 6 H); 1.25 (bs, 60 H); 1.76 (m, 4 H); 3.92 (t, J = 6.5 Hz, 4 H); 6.49 (m, 2 H); 6.51 (m, 1 H); 7.15 (t, J = 8.0 Hz, 1 H); Exact Mass (FAB): Calculated: 614.6002; Found: 614.6015 (+2.2 ppm).

**1,3-Diiodo-4,6-Bisoctadecyloxybenzene (43).** Red mercuric oxide (2.409 g, 11.12 mmol), iodine (2.832 g, 11.16 mmol), **42** (2.22 g, 3.61 mmol) and methylene chloride (35 ml) were stirred together overnight at room temperature. The mixture was filtered and the filter cake washed well with

warm chloroform. The filtrate was washed with 10% $Na_2S_2O_3$ (50 ml), water (50 ml), dried over $MgSO_4$ and passed through a short column of silica gel. Recrystallization from chloroform/methanol afforded 2.75 g (88%) of pure diiodide. mp 88-89°C; $^1$H NMR δ 0.88 (t, J = 6.5 Hz, 6 H); 1.25 (bs, 60 H); 1.83 (m, 4 H); 3.98 (t, J = 6.5 Hz, 4 H); 6.31 (s, 1 H); 8.02 (s, 1 H); $^{13}$C NMR δ 14.14; 22.69; 26.00; 28.97; 29.26; 29.36; 29.53; 29.57; 29.66; 29.70; 31.92; 69.46; 75.94; 97.74; 146.54; 158.96; Anal. Calcd for $C_{42}H_{76}I_2O_2$: C, 58.19; H, 8.84. Found: C, 58.22; H, 8.41; Exact Mass (FAB): Calculated: 866.3935; Found: 866.3930 (-0.6 ppm).

**5,5'Bis(Trimethylstannyl)-2,2':5',2"-Terthiophene (44).** Terthiophene (490 mg, 1.972 mmol) was dissolved in anhydrous diethyl ether (20 ml) and the solution cooled to 0°C. *n*-BuLi (2.37 M, 2.2 ml, 5.21 mmol) was added dropwise via syringe forming a yellow suspension. The mixture was refluxed for ninety minutes and cooled to room temperature. A solution of trimethylstannyl chloride in THF (1.0 M, 6.2 ml, 6.2 mmol) was added, and the mixture stirred for 18 hours. It was then added to saturated $NH_4Cl$ and the layers separated. The organic layer was dried over $MgSO_4$ and concentrated. Recrystallization of the residue from ethanol/hexanes (twice) yielded 659 mg (58%) of bistrimethylstannane as yellow crystals. mp 119-121°C; $^1$H NMR δ 0.39 (s, 18 H); 7.07 (m, 2 H); 7.09 (d, J = 3.4 Hz, 2 H); 7.27 (d, J = 3.4 Hz, 2 H); $^{13}$C NMR δ -8.21; 124.14; 124.77; 135.89; 136.08; 137.54; 142.70; Anal. Calcd for $C_{18}H_{24}S_3Sn_2$: C, 37.67; H, 4.21. Found: C, 37.97; H, 4.43; Exact Mass (FAB): Calculated for $C_{18}H_{24}S_3{}^{118}Sn^{122}Sn$: 574.9104; Found: 574.9101 (-0.6 ppm).

**Polymer 45.** Diiodide **43** (478.2 mg, 0.5516 mmol), **44** (307.1 mg, 0.5350 mmol) and $Pd(PPh_3)_2Cl_2$ (12 mg, 3%) were combined in a 25 ml three-necked flask. Anhydrous THF (10 ml) was added, the mixture stirred at 50°C for 1 hour and then refluxed under argon. The reaction mixture slowly darkened

and after 24 hours additional distannane ((27.8 mg, 0.048 mmol) was added. Reflux continued for 5 days and the mixture was cooled and filtered through celite. It was then concentrated, soxhlet extracted with acetone for 3 days to yield 387.5 mg (84%) of **45** as a red solid. GPC: $M_n$ = 2000, $M_w$ = 6020, PDI = 3.01, (MW of monomer = 859); UV($CH_2Cl_2$) $\lambda_{max}$ = 443 nm.

**1,3-Bisdecyloxybenzene (46).** Resorcinol (10.15 g, 0.092 mol), potassium carbonate (74.5 g, 0.539 mol) and 1-bromodecane (48.0 g, 0.217 mol) were refluxed together in acetonitrile (500 ml) for 20 hours with mechanical stirring and then hot gravity filtered. The mother liquor was concentrated, redissolved in methylene chloride, passed through a short column of silica gel and recrystallized from methylene chloride/methanol to yield 28.34 g (79%) of pure **46**. mp 51-52°C; $^1$H NMR δ 0.88 (t, J = 6.8 Hz, 6 H); 1.27 (s, 28 H); 1.77 (t, J = 7.2 Hz, 4 H); 3.93 (t, J = 6.5 Hz, 4 H); 6.46 (s, 2 H); 6.49 (s, 1 H); 7.15 (t, J = 7.8 Hz, 1H); $^{13}$C NMR δ 14.09; 22.69; 26.09; 29.31; 29.42; 29.60; 31.92; 67.97; 101.50; 106.65; 129.70; 160.41; EIMS, m/z 390(M,37); 250(13); 110(100).

**1,3-Bisdecyloxy-4,6-dibromobenzene (47).**[104] To a solution of **46** in carbon tetrachloride (20 ml) was added a solution of bromine in carbon tetrachloride (1.0 M, 10.5 ml) dropwise at 0°C. The pale yellow solution was allowed to stir for a further thirty minutes at room temperature, added to 10% $Na_2S_2O_3$ (50 ml) and washed with aqueous $NaHCO_3$. The layers were separated, the aqueous layer extracted with diethyl ether and dried over $MgSO_4$. Recrystallization from methylene chloride/methanol furnished 2.102 g (75%) of pure dibromide. mp 55-56°C; $^1$H NMR δ 0.88 (t, J = 6.7 Hz, 6 H); 1.27 (s, 28 H); 1.83 (t, J = 7.2 Hz, 4 H); 3.98 (t, J = 6.5 Hz, 4 H); 6.45 (s, 2 H); 7.64 (s, 1 H); $^{13}$C NMR δ 14.07; 22.66; 25.93; 29.05; 29.30; 29.52; 31.89; 67.67; 99.91; 103.00; 135.69; 155.63; EIMS, m/z 550(M, 5); 548(M, 9); 548(M, 5); 546(M, 5); (268,100); (57,32); (55,57).

**1,3-Bisdecyloxy-4,6-benzene-bisboronic acid (48).** To a solution of **47** (5.400 g, 9.846 mmol) in dry $Et_2O$ (80 ml) was slowly added a solution of *n*-BuLi in hexanes (2.45 M, 14 ml) at -78°C. The mixture was warmed to room temperature, stirred for two hours and recooled to -78°C. Trimethyl borate (10.9 g, 0.105 mol) was added and the mixture stirred for 12 hours at room temperature. It was then partitioned between 10% HCl (200 ml) and diethyl ether, dried over $MgSO_4$ and concentrated to yield 1.847 g (39%) of bisboronic acid. $^1$H NMR δ 0.88 (t, J = 6.8 Hz, 6 H); 1.27 (s, 28 H); 1.85 (m, 4 H); 4.09 (t, J = 6.5 Hz, 4 H); 5.78 (s, 4 H); 6.40 (s, 1 H); 8.27 (s, 1 H).

**References**

(1) *Research Frontiers in Magnetochemistry*; O'Connor, C. J., Ed.; World Scientific Publishing Co.: Singapore, 1993, pp 415.

(2) *Magnetic Molecular Materials*; Gatteschi, D.; Kahn, O.; Miller, J. S.; Palacio, F., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991.

(3) *Chemistry and Physics of Molecular Based Magnetic Materials. Mol. Cryst. Liq. Cryst.*; Iwamura, H.; Miller, J. S., Ed.; Gordon and Breach Publishers: USA, 1993; Vol. 232, pp 360.

(4) Fukutome, H.; I., T.; Ozaki, M. *Chem. Phys. Lett.* **1987**, *133*, 34-38.

(5) Wasserman, E.; Schueller, K.; Yager, W. A. *Chem. Phys. Lett.* **1968**, *2*, 259-260.

(6) Itoh, K. *Pure & Appl. Chem.* **1978**, *50*, 1251-1259.

(7) Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242-248.

(8) Coms, F. D.; Dougherty, D. A. *Tetrahedron Lett.* **1988**, *29*, 3753-3756.

(9) Pranata, J.; Dougherty, D. A. *J. Phys. Org. Chem.* **1989**, *2*, 161-176.

(10) Jain, R.; Sponsler, M. B.; Coms, F. D.; Dougherty, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 1356-1366.

(11) Kato, S.; Morokuma, K.; Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1983**, *105*, 1791-1795.

(12) Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.* **1981**, *14*, 69-76.

(13) Goldberg, A. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 284-290.

(14) By a Boltzmann analysis, singlet (S) and triplet (T) states are equally populated at a temperature in excess of 5000 K if the S-T gap is 10 kcal/mol.

(15) *Handbook of Conducting Polymers, Vol. 1*; Skotheim, T. A., Ed.; Marcel Dekker, Inc.: New York, 1986; Vol. 1, pp 1-726.

(16) *Handbook of Conducting Polymers, Vol. 2*; Skotheim, T. A., Ed.; Marcel Dekker, Inc.: New York, 1986; Vol. 2, pp 729-1417.

(17) Tourillon, G.; Garnier, F. *J. Electrochem. Soc., Electrochem. Sci. Tech.* **1983**, *53*, 2042.

(18) Jen, K. Y.; Maxfield, M.; Shacklette, L. W.; Elsenbaumer, R. L. *J. Chem. Soc. Chem. Commun.* **1987**, 309.

(19) Van-Catledge, F. A. *J. Org. Chem.* **1980**, *45*, 4801.

(20) Nagels, P.; Krikor, H.; Rotti, M. *Synthetic Metals* **1989**, *29*, E29-E34.

(21) Shacklette, L. W.; Elsenbaumer, R. L.; Chance, R. R.; Eckhardt, H.; Frommer, J. E.; Baughman, R. H. *J. Chem. Phys.* **1981**, *75*, 1919.

(22) Swager, T. M.; Grubbs, R. H. *J. Amer. Chem. Soc.* **1987**, *109*, 894-896.

(23) Pranata, J.; Dougherty, D. A. *Synthetic Metals* **1987**, *22*, 171-178.

(24) Khanna, R. K.; Jiang, Y. M.; Srinivas, B.; Smithhart, C. B.; Wertz, D. L. *Chem. Mater.* **1993**, *5*, 1792-1798.

(25) Bally, T.; Roth, K.; Tang, W.; Schrock, R. R.; Knoll, K.; Park, L. Y. *J. Amer. Chem. Soc.* **1992**, *114*, 2440-2446.

(26) Horowitz, G.; Yassar, A.; von Bardeleben, H. J. *Synthetic Metals* **1994**, 245-252.

(27) Jacobs, S. J.; Shultz, D. A.; Jain, R.; Novak, J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 1744-1753.

(28) Davies, A. G.; Julia, L.; Yazdi, S. N. *J. Chem. Soc. Chem. Commun.* **1987**, 929.

(29) Davies, A. G.; Julia, L.; Yadzi, S. N. *J. Chem. Soc. Chem. Perkin Trans. II* **1989**, 239.

(30) Aleman, C.; Brillas, E.; Davies, A. G.; Kajari, L.; Giro, D.; Julia, L. L.; Perez, J. J.; Rius, J. *J. Org. Chem.* **1993**, *58*, 3091-3099.

(31) Zotti, G.; Schiavon, G. *Chem. Mater.* **1991**, *3*, 62-65.

(32) Child, A. D.; Reynolds, J. R. *J. Chem. Soc. Chem. Commun.* **1991**, 1779-1791.

(33) Miller, J. S. *Adv. Mater.* **1992**, *4*, 435-438.

(34) Torrance, J. B.; Oostra, S.; Nazzal, A. *Synthetic Metals* **1987**, *19*, 709-714.

(35) Ota, M.; Otani, S.; Igarashi, M. *Chem. Lett.* **1989**, 1183-1186.

(36) Winokur, M. J.; Spiegel, D.; Kim, Y.; Hotta, S.; Heeger, A. J. *Synthetic Metals* **1989**, *28*, C419-C426.

(37) Jozefiak, T. H.; Ginsburg, E.; Gorman, C. B.; Grubbs, R. H.; Lewis, N. L. *J. Amer. Chem. Soc.* **1993**, *115*, 4705-4713.

(38) Chen, S. A.; Ni, J. M. *Macromolecules* **1992**, *25*, 6081.

(39) Allcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry;* Second ed.; Prentice-Hall: New Jersey, 1990, pp 1-624.

(40) Kaisaki, D. A.; Chang, W.; Dougherty, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 2764-2766.

(41) McDonald, R. N.; Campbell, T. W. *J. Amer. Chem. Soc.* **1960**, *82*, 4669-4671.

(42) Kossmehl, G.; Härtel, M.; Manecke, G. *Macromol. Chem.* **1970**, *131*, 15.

(43) Gourley, K. D.; Lillya, C. P.; Reynolds, J. R.; Chien, J. C. *Macromolecules* **1984**, *17*, 1025.

(44) Yen, K. Y.; Cava, M. P.; Huang, W. S.; MacDiarmaid, A. G. *J. Chem. Soc. Chem. Commun.* **1983**, 1502.

(45) March, J. *Advanced Organic Chemistry;* Fourth ed.; John Wiley and Sons Inc.: New York, 1992, pp 956-963.

(46) Kossmehl, G.; Samandari, M. *Makromol. Chem.* **1983**, *184*, 2437-2445.

(47) Sone, T. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1197-1200.

(48) Feringa, B. L.; Hulst, R.; Rikas, R.; Brandsma, L. *Synthesis* **1988**, 316.

(49) Nakayama, J.; Fujimori, T. *Sulfur Lett.* **1990**, *11*, 29.

(50) Percec, V.; Hill, D. H. *ACS Symposium Series* **1996**, *624*, 2-56.

(51) Kumada, M. *Pure Appl. Chem.* **1980**, *52*, 669.

(52) Stille, J. K. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508.

(53) Mitchell, T. M. *Synthesis* **1992**, 803.

(54) Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340.

(55) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.

(56) Rehahn, M.; Schlüter, A.-D.; Wegner, G.; Feast, W. J. *Polymer* **1989**, *30*, 1060-1062.

(57) Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 7411-7412.

(58) Goldfinger, M. B.; Swager, T. M. *J. Amer. Chem. Soc.* **1994**, *116*, 7895.

(59) Kim, Y. H.; Webster, O. W. *J. Am. Chem. Soc.* **1990**, *112*, 4592-4593.

(60) Lock, G.; Schreckeneder, R. *Chem. Ber.* **1939**, *72*, 511.

(61) Doyle, M. P.; Dellaria, J. F. J.; Siegfried, B.; Bishop, S. W. *J. Org. Chem.* **1977**, *42*, 3494.

(62) Haubold, W.; Herdtle, J.; Gollinger, W.; Einholz, W. *J. Organometallic Chem.* **1986**, *315*, 1.

(63) Miller, T. M.; Neenan, T. X.; Zayas, R.; Bair, H. E. *J. Amer. Chem. Soc.* **1992**, *114*, 1018.

(64) Hyuga, S.; Yamashina, N.; Hara, S.; Suzuki, A. *Chem. Lett.* **1988**, 809.

(65) Kaisaki, D. A. Thesis, California Institute of Technology, Pasadena, California, 1990.

(66) Iwamura, H.; Koga, N. *Acc. Chem. Res.* **1993**, *26*, 346-351.

(67) Gerloch, M. *Magnetism and Ligand-Field Analysis*; Cambridge University Press: New York, 1983.

(68) Jacobs, S. J. Thesis, California Institute of Technology, Pasadena, California, 1994.

(69) Murray, M. M.; Kaszynski, P.; Kaisaki, D. A.; Chang, W.; Dougherty, D.

A. *J. Am. Chem. Soc.* **1994**, *116*, 8152-8161.

(70) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: New York, 1986, pp 1-328.

(71) Rajca, A.; Utamapanya, S. *J. Am. Chem. Soc.* **1993**, *115*, 10688-10694.

(72) Pron, A.; MacDiarmaid, A. G.; Heeger, A. J. *Materials Science* **1981**, *VII*, 313.

(73) Hill, M. G.; Mann, K. R.; Miller, L. L.; Penneau, J. F.; Zinger, B. *Chem. Mater.* **1992**, *4*, 1106.

(74) Hill, M. G.; Mann, K. R.; Miller, L. L.; Penneau, J. F. *J. Amer. Chem. Soc.* **1992**, *114*, 2728.

(75) Scaling the Hückel spin density at the benzylic positions from Table 2.1 by the singlet-triplet gap of m-xylylene (10 kcal/mol) gives a gap of 220 cal/mol. This corresponds to a temperature of ca. 110 K for the onset of ferromagnetic coupling.

(76) Anderson, K. K. Thesis, California Institute of Technology, Pasadena, California, 1996.

(77) Clites, J. A., California Institute of Technology, personal communication.

(78) Kaszynski, P.; Dougherty, D. A. *J. Org. Chem.* **1993**, *58*, 5209-5220.

(79) March, J. *Advanced Organic Chemistry;* Fourth ed.; John Wiley and Sons Inc.: New York, 1992, pp 433-435.

(80) Bäurle, P. *Adv. Mater.* **1992**, *4*, 102.

(81) Guay, J.; Diaz, A.; Wu, R.; Tour, J. M. *Chem. Mater.* **1992**, *4*, 254-255.

(82) Guay, J.; Diaz, A.; Wu, R.; Tour, J. M. *J. Amer. Chem. Soc.* **1993**, *115*, 1869-1874.

(83) Dietrich, M.; Heinze, J. *J. Amer. Chem. Soc.* **1990**, *112*, 5142-5145.

(84) Hünig, S.; Steinmetzer, H.-C. *Liegibs Ann. Chem.* **1976**, 1090-1102.

(85) McCullough, R. D.; Williams, S. P. *J. Amer. Chem. Soc.* **1993**, *115*, 11608.

(86) Marsella, M. J.; Newland, R. J.; Carroll, P. J.; Swager, T. M. *J. Amer. Chem. Soc.* **1995**, *117*, 9842.

(87) Yu, Y.; Gunic, E.; Miller, L. L. *Chem. Mater.* **1995**, *7*, 255.

(88) Marsella, M. J., California Institute of Technology, personal communication.

(89) Miller, L. L.; Yu, Y. *J. Org. Chem.* **1995**, *60*, 6813.

(90) Yu, Y.; Gunic, E.; Zinger, B.; Miller, L. L. *J. Amer. Chem. Soc.* **1996**, *118*, 1013.

(91) Marsella, M. J.; Carroll, P. J.; Swager, T. M. *J. Amer. Chem. Soc.* **1995**, *117*, 9832.

(92) Baizer, M. M.; Lund, H. *Organic Electrochemistry;* Second ed.; Marcel Dekker, Inc.: New York, 1983, pp 1-1166.

(93) Rai, R.; Aubrecht, K. B.; Collum, D. B. *Tett. Lett.* **1995**, *36*, 3111-3114.

(94) Ikenoue, Y.; Chiang, J.; Patil, A. O.; Wudl, F.; Heeger, A. J. *J. Amer. Chem. Soc.* **1988**, *110*, 2983.

(95) Isabel Arroyo-Villan, M.; Diaz-Quijada, G. A.; Abdou, M. S. A.; Holdcroft, S. *Macromolecules* **1995**, *28*, 975.

(96) Child, A. D.; Reynolds, J. R. *Macromolecules* **1994**, *27*, 1975.

(97) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(98) Spartan Version 2.1 (1992) Wavefunction, Inc., Irvine, CA.

(99) Bao, Z.; Chan, W. K.; Yu, L. *J. Amer. Chem. Soc.* **1995**, *117*, 12426.

(100) Yoshizawa, K.; Chano, A.; Ito, A.; Tanaka, K.; Yamabe, T.; Fujita, H.; Yamauchi, J.; Shiro, M. *J. Am. Chem. Soc.* **1992**, *114*, 5995-5998.

(101) Nakamura, N.; Inoue, K.; Iwamura, H. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 872-874.

(102) Nishide, H.; Kaneko, T.; Nii, T.; Katoh, K.; Tsuchida, E.; Yamaguchi, K. *J. Amer. Chem. Soc.* **1995**, *117*, 548.

(103) Rutherford, D. R.; Stille, J. K.; Elliot, C. M.; Reichert, V. R. *Macromolecules* **1992**, *25*, 2294.

(104) Ruiz, J. P.; Dharia, J. R.; Reynolds, J. R. *Macromolecules* **1992**, *25*, 849.

# Chapter 3. Viologens as Room Temperature Stable Radical Cations for High-Spin Magnetic Materials

**Introduction**

An apparently very stable class of radical cations is the group of *N,N'*-dialkylbipyridiniums. Two well-known members of this category are the commercial herbicides "paraquat", (**3-1**), where R=$CH_3$, and "diquat" (**3-2**) (Figure 3-1).

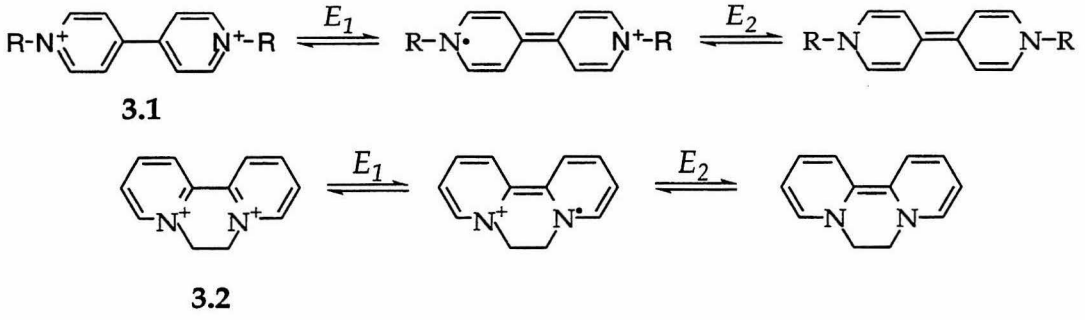



**Figure 3-1.** Electrochemical reversibility of paraquat and diquat.

They are bipyridyl bisquaternary salts and share several common characteristics:

- Both may transfer two electrons stepwise in a reversible manner. They exhibit what is described as "Weitz type" behavior: their fully reduced forms are quinoid or polyenic by nature, whereas they can be considered to be aromatic in the fully oxidized form.[1] This class of materials possess one of the lowest (most cathodic) redox potentials of any organic system displaying a significant degree of reversibility.[2]
- Their radical cations are highly colored, paraquat is often termed methyl viologen because of the intense purple color of its radical cation.
- They are soluble in water but can be dissolved in polar organic solvents by appropriate ion-exchange.

The unique properties of these systems have been exploited in the

development of photoelectric cells, light-emitting diodes,[2] and optical memory devices.[3] In addition, methyl viologen serves as a useful enzyme redox mediator because of its unique solubility properties and rapid electron transfer.

It was considered that redox systems of this type would prove very useful spin sources for the polaronic ferromagnet paradigm as described in Chapter 2. Early studies employed a chemical oxidation protocol to generate spin carriers.[4] A significant limitation to this approach is that doped and undoped polymeric systems have different solubility requirements: neutral polymeric hydrocarbons are soluble in low dielectric solvents, whereas the polyions produced upon doping are insoluble in these solvents. Polymers precipitate out of solution as oxidation proceeds and this interferes with the doping process. Bipyridiniums, however, are charged in both their singly-reduced and oxidized forms and retain their solubility upon chemical or electrochemical reduction. Electrochemical doping seems especially attractive in these systems as the redox processes $E_1$ and $E_2$ are well-separated. This is important because all redox couples of this type are subject to disproportionation reactions either in solution or at an electrode.

$$V^{2+} \underset{}{\overset{E_1}{\rightleftharpoons}} V^{+\bullet} \overset{E_2}{\rightleftharpoons} V^0 \qquad (1)$$

$$2V^{+\bullet} \longrightarrow V^{2+} + V^0 \quad \text{(disproportionation)} \qquad (2)$$

$$V^{2+} + V^0 \longrightarrow 2V^{+\bullet} \quad \text{(conproportionation)} \qquad (3)$$

The conproportionation equilibrium constant, $K_{conp}$, may be related to the difference in redox potentials $E_1$ and $E_2$ by:

$$E_2 - E_1 = \frac{RTlnK_{conp}}{F} \qquad (4)$$

$$K_{conp} = \frac{[V^{+\bullet}]^2}{[V^0][V^{2+}]} \quad (5)$$

where $V^{\bullet+}$, $V^0$, and $V^{2+}$ are the semi-reduced, fully reduced and oxidized forms of the redox couples respectively. Thus, the conproproportionation constant is approximately $10^6$ for these systems.[5]

**Synthetic Strategy**

Our ultimate goal was the synthesis of a hyperbranched poly(viologen) structure as depicted in Figure 3-2. Viologens, e.g., **3.1** or **3.2**, serve as robust SCs high-spin coupled *meta* through a benzene. Such a highly charged macromolecule is expected to show novel solubility and electron transfer properties.

How could we synthesize such a structure? We initially targeted **3.1** as a potential SC for the polaronic ferromagnet. Connection through nitrogen appeared to be optimal as most spin density is thought to reside on the heteroatom.

There was some literature precedent for the synthesis of *N,N*-biaryl-4,4-bipyridinium salts by exchange with 1-chloro-2,4-dinitro pyridinium salts in aqueous media (Scheme 3-1).[6-8] The synthesis of a model triplet radical precursor was then attempted using this methodology. Treatment of 4,4'-bipyridyl with 1-chloro-2,4-dinitrobenzene in acetonitrile or methanol yielded **3.3** (Scheme 3-2). Amine exchange with excess aniline or *tert*-butyl aniline in water afforded **3.4** in good yield. Conversion of **3.4** to **3.5** is very slow relative to the conversion of 4,4'-dipyridyl to **3.3**, requiring two weeks to

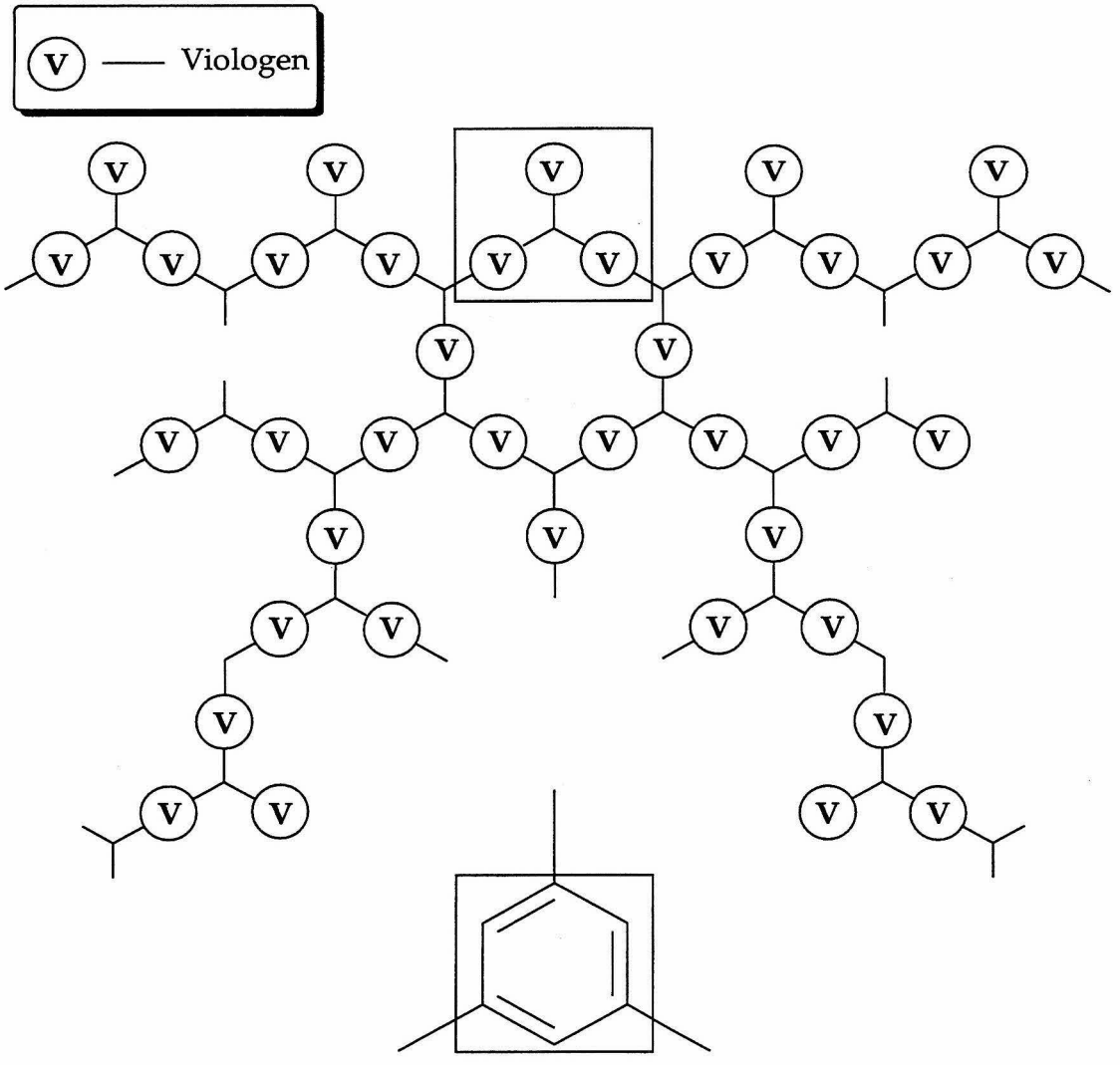
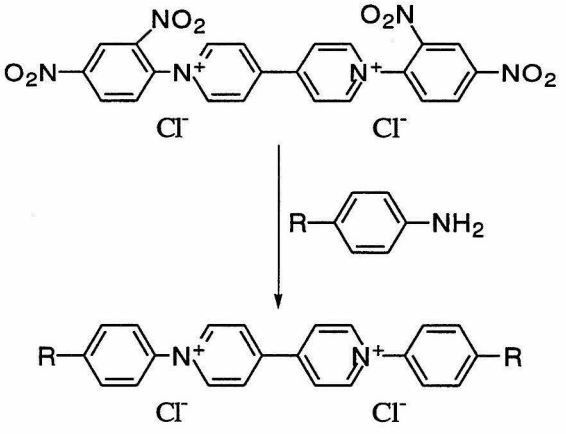


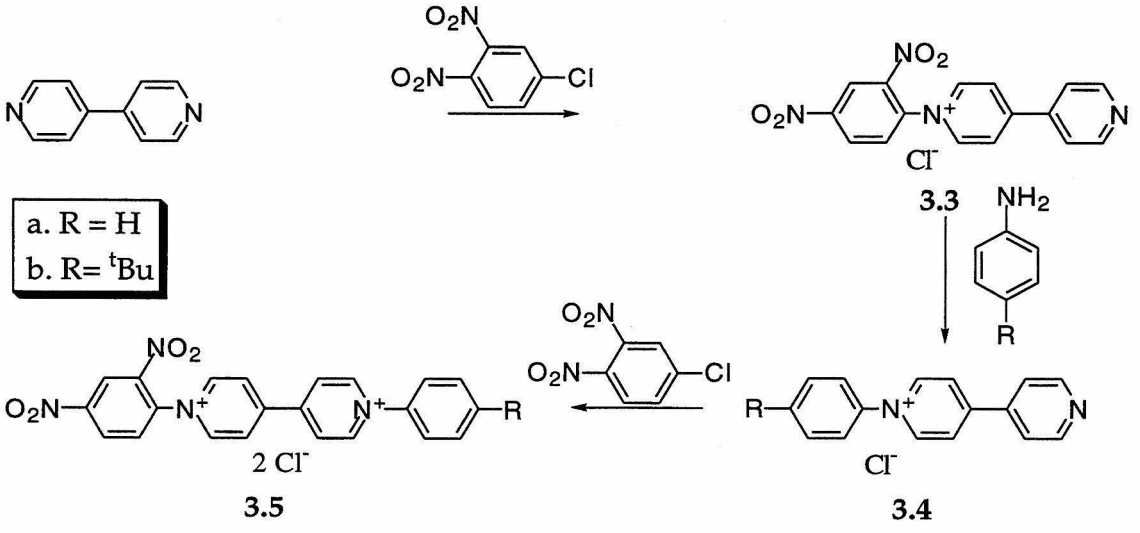

**Figure 3-2.** A target viologen hyperbranched structure.

push the reaction to completion in refluxing acetonitrile. This initial observation did not bode well for future attempts to functionalize monoquaternized 4,4'-dipyridyl at nitrogen.

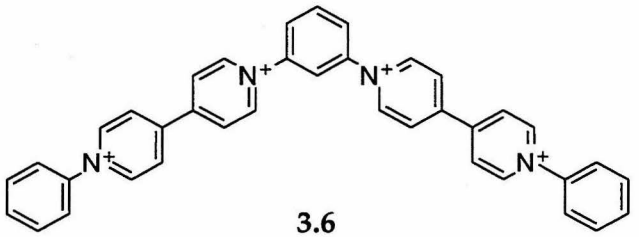
**Scheme 3-1**



**Scheme 3-2**



Attempts to react **3.5a** with 1,3-diaminobenzene in water did not yield any of the desired dimeric compound **3.6**; monosubstituted product was obtained exclusively. **3.5b** was ion-exchanged with $PF_6^-$ to extend its solubility range, and a reaction with 1,3-diaminobenzene was conducted in warm (140°C) benzonitrile. $^1H$ NMR spectra of the reaction mixture taken after 2 days and 9 days were identical and were consistent with only starting material and monosubstituted product. It became abundantly clear at this stage that the amine exchange reaction would not be a viable means of synthesizing structures such as those depicted in Figure 3-2 and this synthetic route was abandoned.

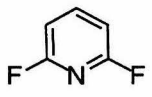


**3.6**

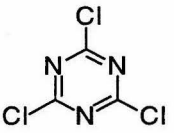
The results obtained here are entirely consistent with observations of other researchers: electron deficient amines undergo the amine exchange reaction sluggishly. 3-Nitroaniline and 4-cyanoaniline furnish the corresponding aryl pyridiniums in 64 and 15% yields respectively, whereas 4-nitroaniline does not react at all.[9] The reaction is best performed in water; the side-product 2,4-dinitroaniline is insoluble in aqueous media and this helps drive the reaction to completion. Other researchers employ a considerable excess of amine to achieve the same objective.[10]

Nucleophilic displacement of readily available highly electron-deficient aromatic halides such as difluoropyridine, **3.7**, cyanuric chloride, **3.8**, or 2,4-dichloropyrimidine, **3.9**, appeared to be an attractive alternative route to

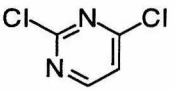
hyperbranched structures incorporating viologens; the ring is activated towards further nucleophilic substitution when it becomes singly charged.



**3.7**



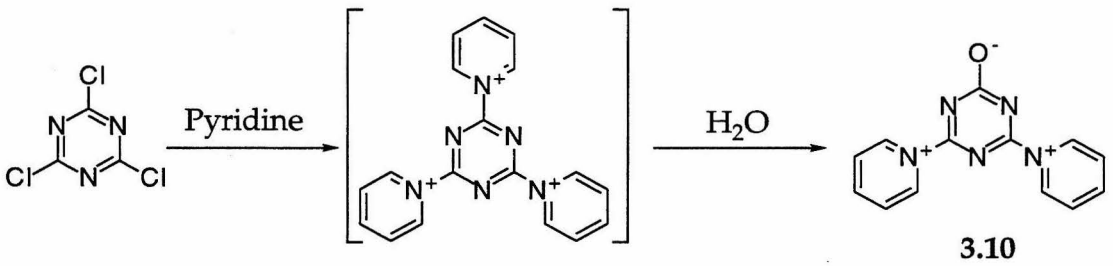
**3.8**



**3.9**

Some model reactions employing pyridine as a nucleophile were initially performed. Difluoropyridine when treated with pyridine in refluxing acetonitrile gave no discernible reaction. Mixing the reagents in warm benzonitrile yielded a black insoluble solid. Cyanuric chloride reacts rapidly with pyridine in acetonitrile at room temperature (Scheme 3-3) but the tripyridinium salt cannot be isolated, as it is only soluble in protic solvents and is readily hydrolyzed to **3.10** as confirmed by $^{13}C$ NMR and IR.[11]

**Scheme 3-3**



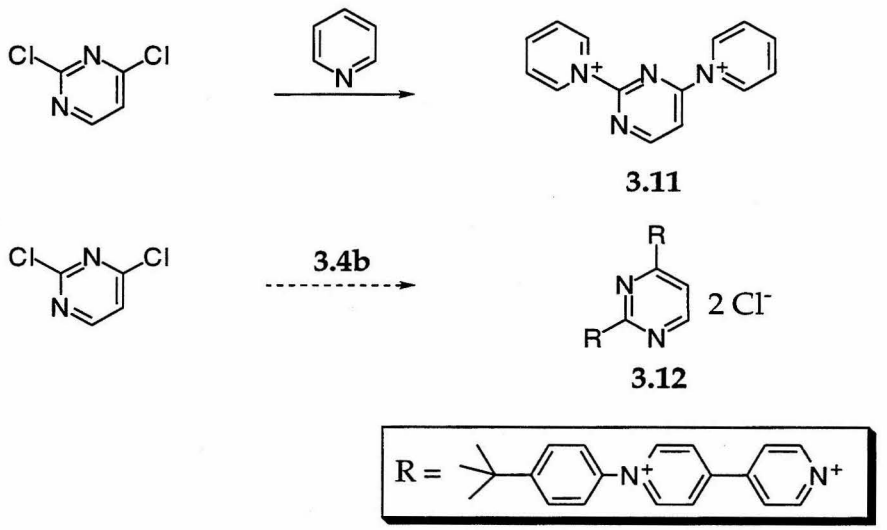

**3.10**

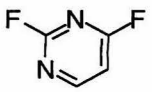
Dichloropyrimidine reacted cleanly with pyridine at reflux temperatures in acetonitrile and the water-soluble bispyridinium salt **3.11** was isolated (Scheme 3-4).[12] A subsequent attempt to react **3.4b** with dichloropyrimidine yielded a small amount of material whose $^1H$ NMR was not inconsistent with **3.12** but the low yield and considerable darkening of the reaction

mixture were troubling.

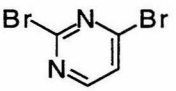
2-4-Difluoropyrimidine,[13] **3.13**, 2,4-dibromopyrimidine[14] **3.14** and 2,4-diiodopyrimidine, **3.15**, were all synthesized and reacted with **3.4a** or **3.4b**. Difluoropyrimidine did not react at all under any of the conditions tried. Dibromopyrimidine and diiodopyrimidine[15] did exhibit increased reactivity relative to dichloride; the NMR spectra of both reaction mixtures showed the characteristic resonances of a bipyridyl-substituted pyrimidine, but also showed a mass of unassignable peaks in the $\delta$ = 7-8 ppm aromatic region, probably due to decomposition of product by ring-opening or some other such mechanism. It is likely that the desired model compound **3.12** could be separated from the reaction mixture by preparative HPLC, but as these initial studies sought to establish reasonable *polymerization* protocols, this avenue was not pursued.

**Scheme 3-4**

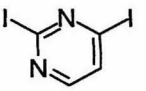




**3.13**



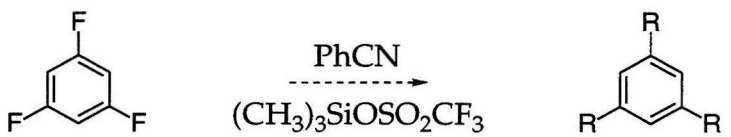
**3.14**



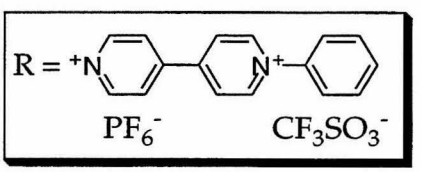
**3.15**

A final attempt to synthesize a model triviologen compound **3.16** by nucleophilic displacement of fluoride was attempted employing the reaction conditions developed by Weiss et al. This protocol was successful in substituting all six fluorines of hexafluorobenzene with pyridines (Scheme 3-5).[16] Again, no desired product was obtained after prolonged reaction in hot benzonitrile in a sealed tube. A similar result was obtained with 2,4,6-trifluoropyrimidine as substrate. This functionalization through nitrogen approach was then abandoned; it became clear that model compounds could not be synthesized in reasonable yield under the harsh conditions required to substitute the first halide.

**Scheme 3-5**



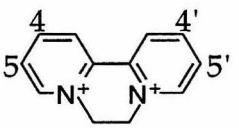

**3.16**




**Diquat Derivatives**

Our attention then turned to possible functionalization of diquat. There are two easily functionalized sites for attachment on the 2,2' bipyridyl

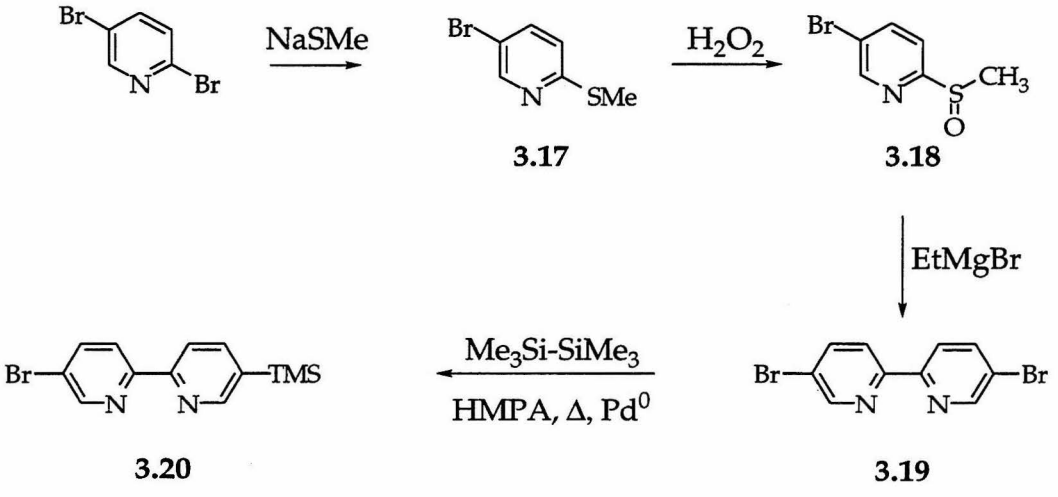
backbone. Early theoretical studies suggested that spin density at the 4 position is greater than at position 5.[17] This argument has been refuted by later experimental studies.[18,19] In any event, halopyridines substituted at the 4-position are prone to polymerization and are of little use for our purposes. Thus, the 5 position was chosen as the point of attachment to the *meta*-phenylene FC.




5,5'-Dibromo-2,2'-bipyridine is a known molecule and was synthesized in three steps by modifying a known procedure .[20,21] Dimerization of viologen radical cations has been documented,[22] and it would be advantageous if this could be suppressed in model systems to allow a more rigorous analysis of magnetic data. Unforeseen difficulties were encountered, however, in endcapping **3.19**. 5,5'-Dibromo-2,2'-bipyridine does not form a stable Grignard reagent and cannot be metallated at low temperature because of its limited solubility in ethereal solvents. All attempts at lithium-halogen exchange at 0°C resulted in destruction of the ring. Attempted Pd(0) mediated Stille coupling with benzyltributyl stannane or nickel-catalyzed coupling with benzylmagnesium chloride also failed. Treatment of **3.19** with phenylboronic acid derivatives was successful but limitations of this approach will be discussed later. Hexamethyldisilane, however, could be coaxed to oxidatively add across the carbon-halide bond in HMPA in the presence of $Pd(PPh_3)_4$. The same reaction conducted in relatively benign DMPU resulted in significantly lower yields. Curiously, a reported procedure employing refluxing xylenes as solvent is successful for 3-bromopyridine but did not

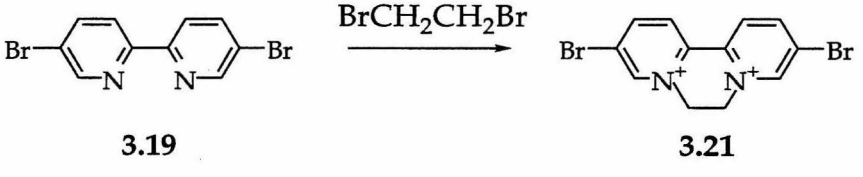
yield anything other than starting material in this case.[23] This suggests that bipyridine behaves as a weakly-bound ligand for the Pd(0) metal center that interferes with the transmetallation reaction; polar solvents promote ligand dissociation.

**Scheme 3-6**




Dibromide **3.19** may be treated with dibromoethane in refluxing nitrobenzene over a period of one week to yield **3.21**. In contrast, the parent 2,2'-bipyridyl may be quaternized in quantitative yield overnight in refluxing dibromoethane.

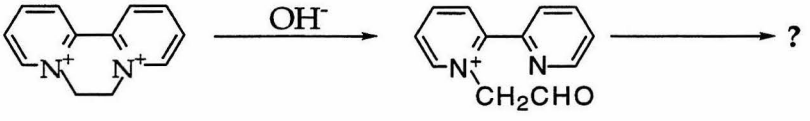
**Scheme 3-7**




A series of Pd-mediated coupling reactions were then performed on **3.21**. It was clear from the outset that standard Suzuki coupling conditions would

not be successful on this substrate.[24] The conversion of diquat to **3.22** and ultimately to other products in aqueous base is documented,[25] and it was expected that **3.21** would be even more susceptible to nucleophilic attack (Scheme 3-8). A number of non-aqueous Suzuki protocols have since been developed and a number of these were attempted.

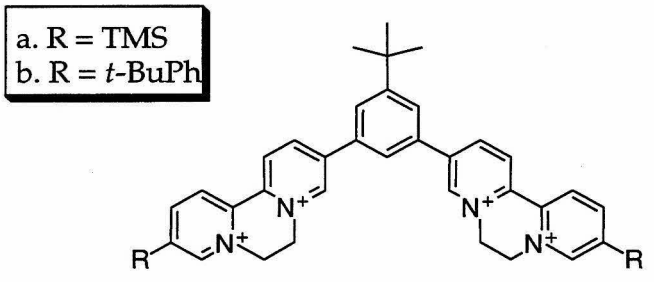
**Scheme 3-8**




**3.22**

Treatment of **3.21** with phenylboronic acid and triethylamine in *N,N'*-dimethylformamide in the presence of $Pd(PPh_3)_4$[26] resulted in complete destruction of starting material. Similar behavior is observed in the absence of base or catalyst and is undoubtedly a consequence of electron transfer. A very mild procedure employing cesium fluoride in acetonitrile has recently been reported.[27] This protocol facilitates cross-coupling of aromatic bromides in the presence of base-labile functional groups such as esters and tosylates. When **3.21** was treated with cesium fluoride and phenylboronic acid, however, immediate decomposition to an insoluble product ensued. Starting phenylboronic acid was recovered as shown by $^1H$ NMR. A final attempt at functionalizing **3.21** was attempted using phenyltributyltin in the presence of Pd(0) and *N,N'*-dimethylformamide.[28-30] Moderate success was achieved in this instance. The reaction was monitored by $^1H$ NMR and appeared to be 33% complete after stirring 24 hours at 120°C. Premature precipitation of metallic Pd and a slow reaction rate were troubling, however.

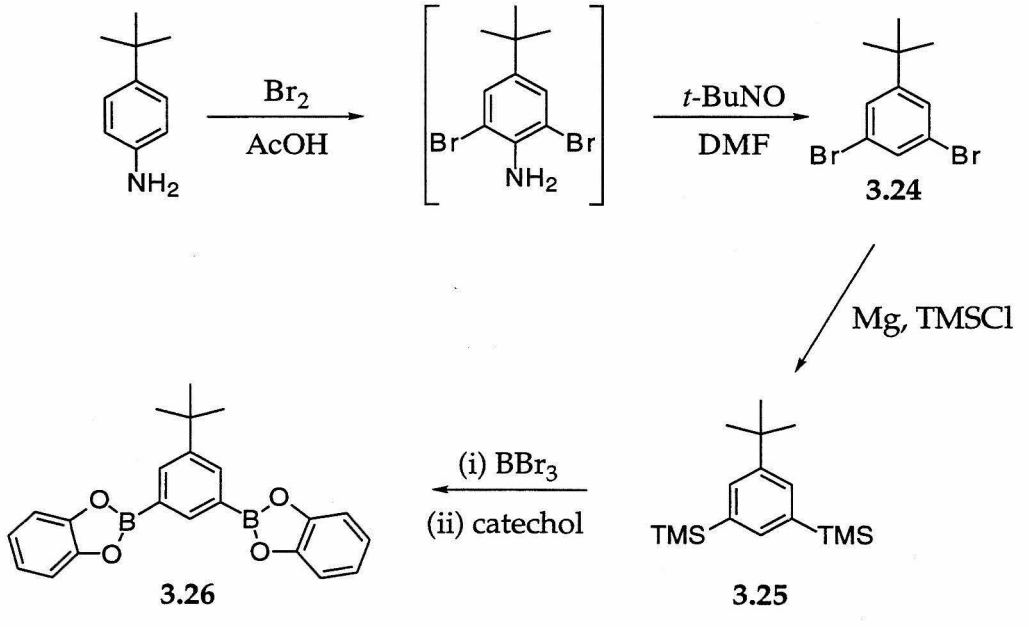
Our attention turned at this point to the synthesis of model compound **3.23** which could be achieved in a stepwise manner.




**3.23**

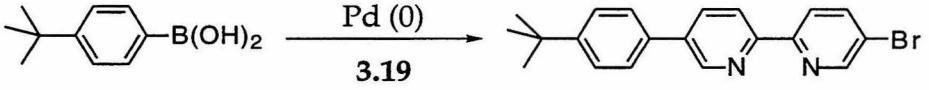
Synthesis of the required 5-*tert*-butyl bisboronic ester closely follows a procedure described for its tetradecyl analog,[31] and is outlined in Scheme 3-9. Incorporation of bulky *tert*-butyl was considered advantageous as its steric bulk may help diminish conproportionation[32] and undesirable intermolecular antiferromagnetic interactions.

**Scheme 3-9**



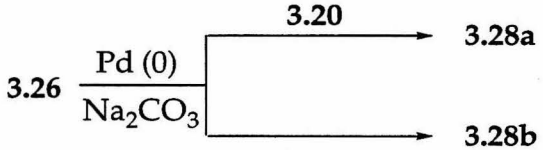
Coupling of bisboronic **3.26** with bromides **3.20** and **3.27** (Scheme 3-10) proceeded smoothly to yield neutral **3.28a** and **3.28b** respectively (Scheme 3-11).

**Scheme 3-10**

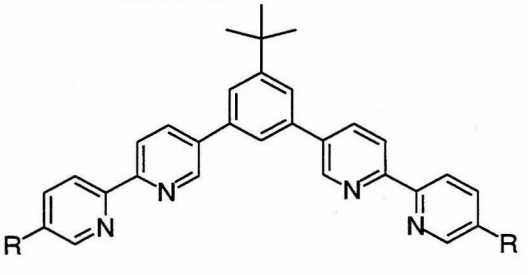



**3.27**

**Scheme 3-11**




a. R = $SiMe_3$
b. R= tert-butyl Ph

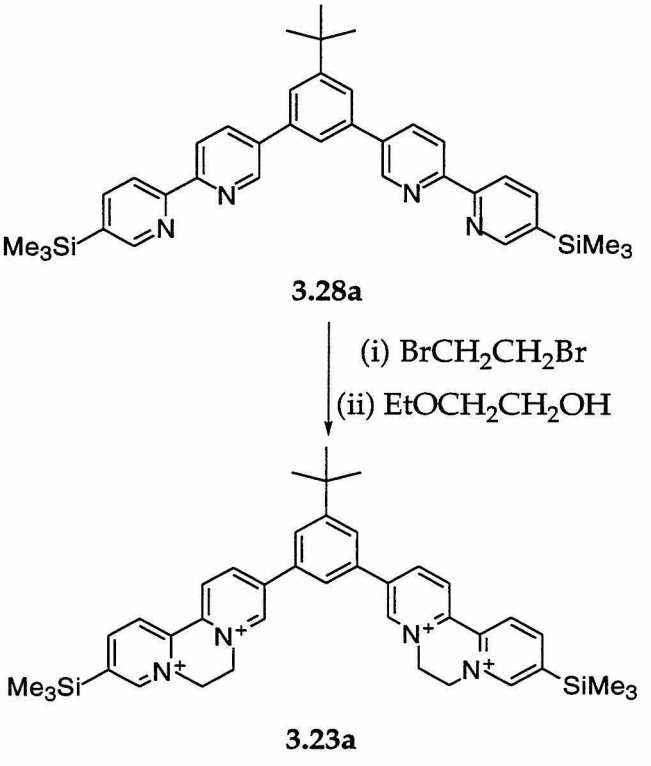



**3.28**

**3.28a** was treated with excess dibromoethane and the resulting precipitate could be redissolved in ethoxyethanol to generate tetracationic **3.23a** which is freely soluble in protic solvents (Scheme 3-12); **3.23b** could not be synthesized

as the initially formed bisquaternized adduct could not be dissolved in any synthetically useful organic solvents. This observation further emphasizes the remarkable ability of trimethylsilyl groups to solubilize organic materials in a range of solvents. The second addition of dibromoethane is far slower than the first, reaction times of several weeks were necessary. Curiously, ethylene glycol di-*p*-tosylate reacted with 2,2'-bipyridyl in the melt but did not yield diquat when the reaction was conducted in solution.

**Scheme 3-12**

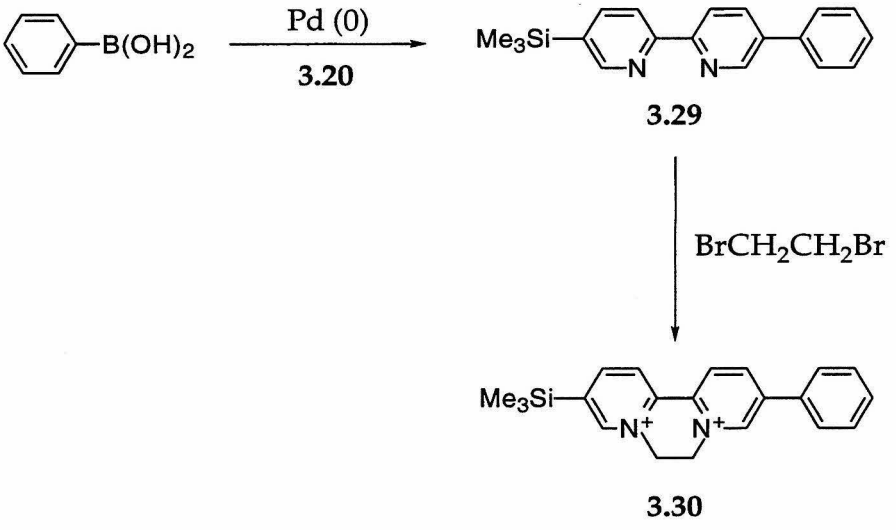



**3.28a**

**3.23a**

The cyclic voltammogram of **3.23a** is depicted in Figure 3-3 and is indistinguishable from the CV of a model compound **3.30** whose synthesis is outlined in Scheme 3-13.

**Scheme 3-13**




The initial reduction wave, $E_1$, is centered at -0.31 V versus Ag/AgCl and is anodically shifted relative to diquat itself ($E_1$ = -0.35 V). This is consistent with the electron-withdrawing nature of phenyl and trimethylsilyl groups.[33] The second reduction wave appears to be quasi-reversible.

In order to familiarize ourselves with the bulk electrolysis of these systems, the bishexafluorophosphate salt of diquat itself was reduced electrochemically in acetonitrile. Surprisingly, the material isolated upon removal of solvent was diamagnetic as shown by SQUID magnetometry. This behavior was observed when both $ClO_4^-$ and $PF_6^-$ were used as counterions. Stability on the cyclic voltammogram scale does not translate into stable spins in the solid state.

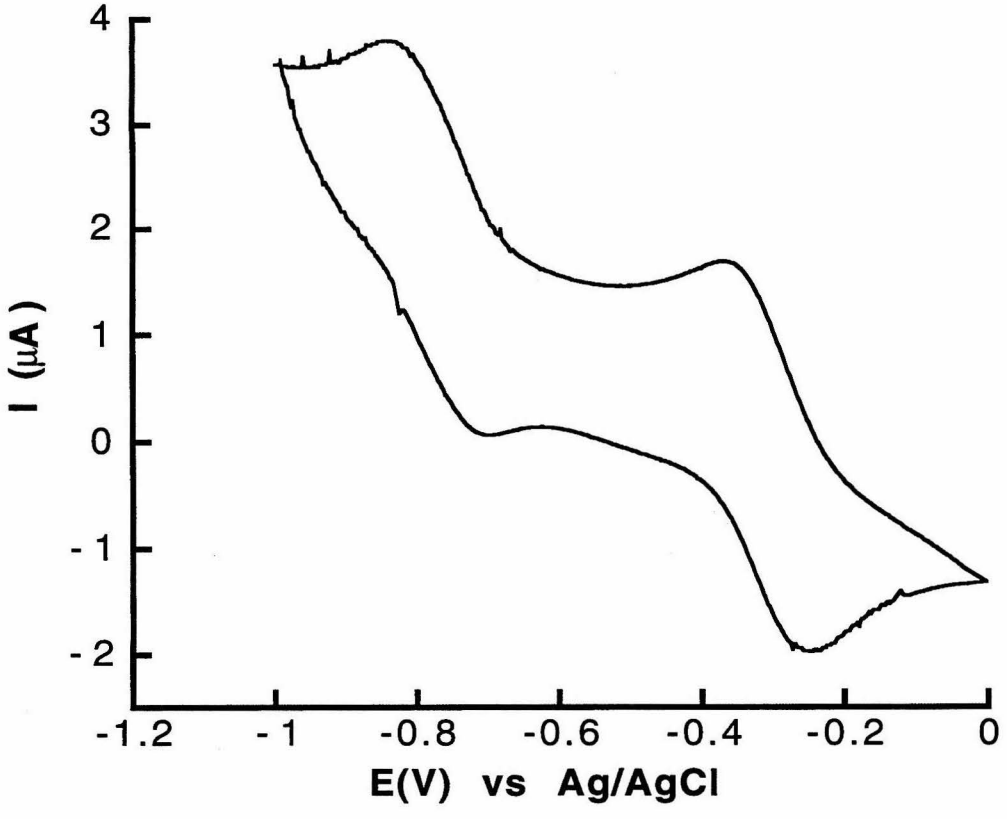



**Figure 3-3.** Cyclic voltammogram for the reduction of **3.23a** in 0.092 M $Bu_4NPF_6/CH_3CN$, $\nu$ = 100mV/s.

Preliminary studies performed on **3.23a**, however, suggest that it may be reduced electrochemically to a stable radical cation. A single experiment was performed: 2 F/mol of electricity was passed through a solution of **3.23a** in acetonitrile while the potential was held at or below $E_1$ = -0.31 V. The solvent was removed under vacuum and the residue subjected to magnetic analysis. Saturation magnetization data suggests that the material best fits to $S$ = 0.9

with a spin concentration of at least 26% (Figure 3-4).

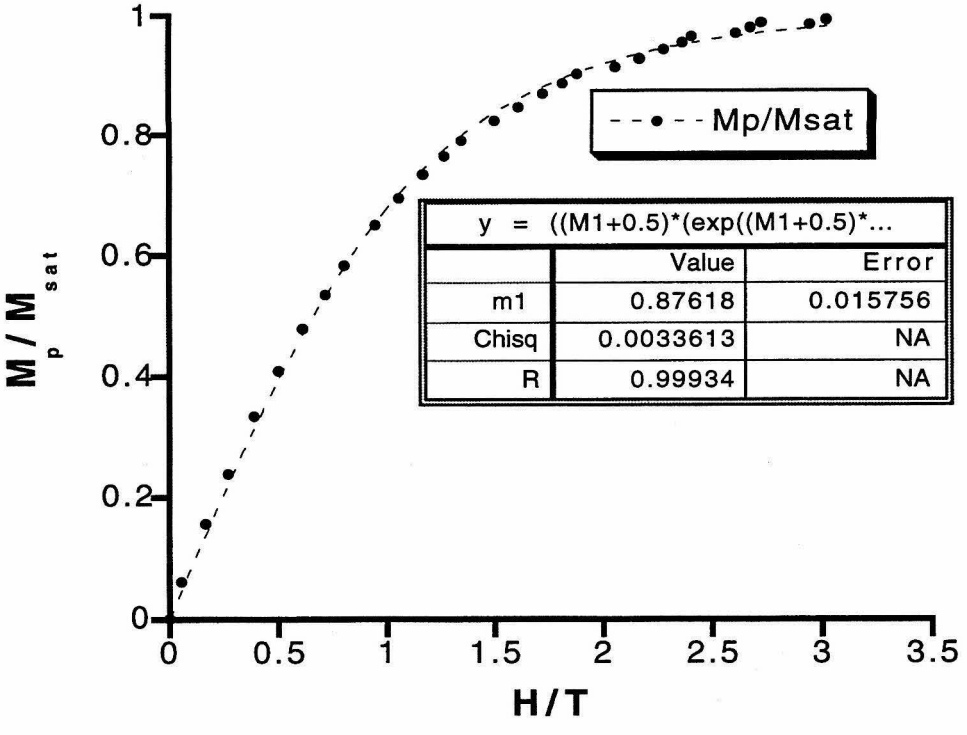



**Figure 3-4.** Best Brillouin fit to magnetization data of electrochemically reduced **3.23a**.

The spin count is considered a lower limit in this preliminary experiment as considerable difficulty was experienced in removing adsorbed solvent. The variable temperature data was similar to other systems studied. The effective moment data above 200 K is very scattered and is not included. It is interesting to note that deleterious antiferromagnetic interactions appear to be of similar magnitude to polymeric systems discussed in Chapter 2. No definitive upturn in magnetic moment is observed although this is to be expected given the relatively low *S* value. In addition, since the spin density

at the benzylic position is estimated to be 0.15,[19] the upturn in effective moment is expected to be in the 200-300 K regime. The absolute paramagnetic moment is often very small at these temperatures for our systems and subtle changes in effective moment may be undetectable, as discussed in Chapter 2.

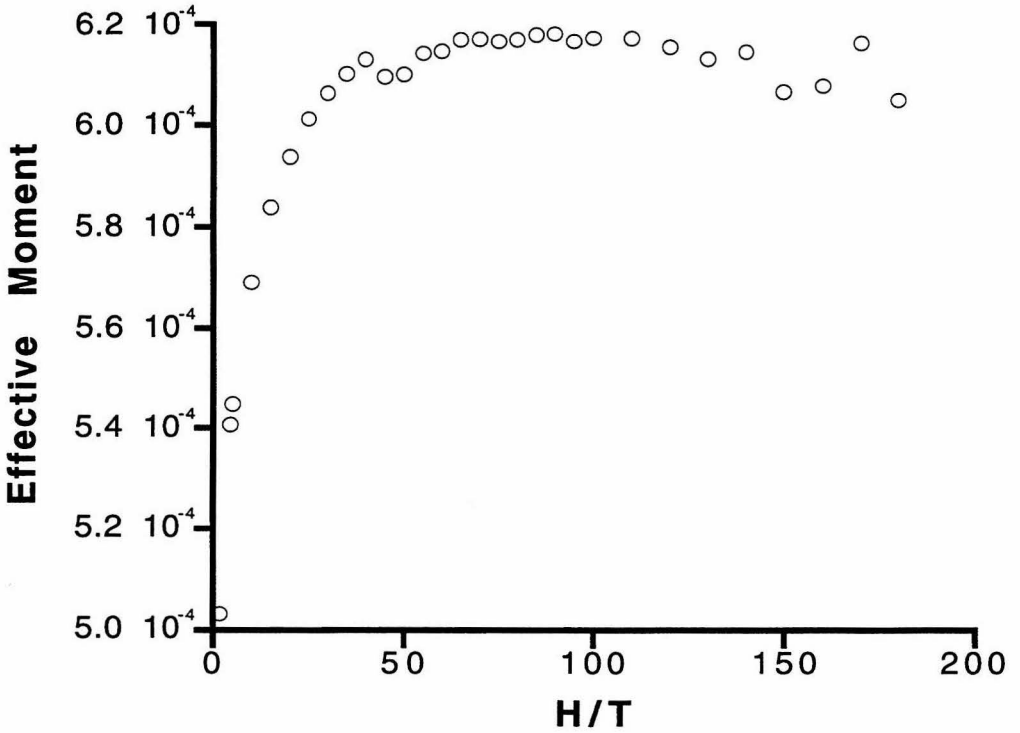



**Figure 3-5.** Effective moment plot of electrochemically reduced **3.23a**.

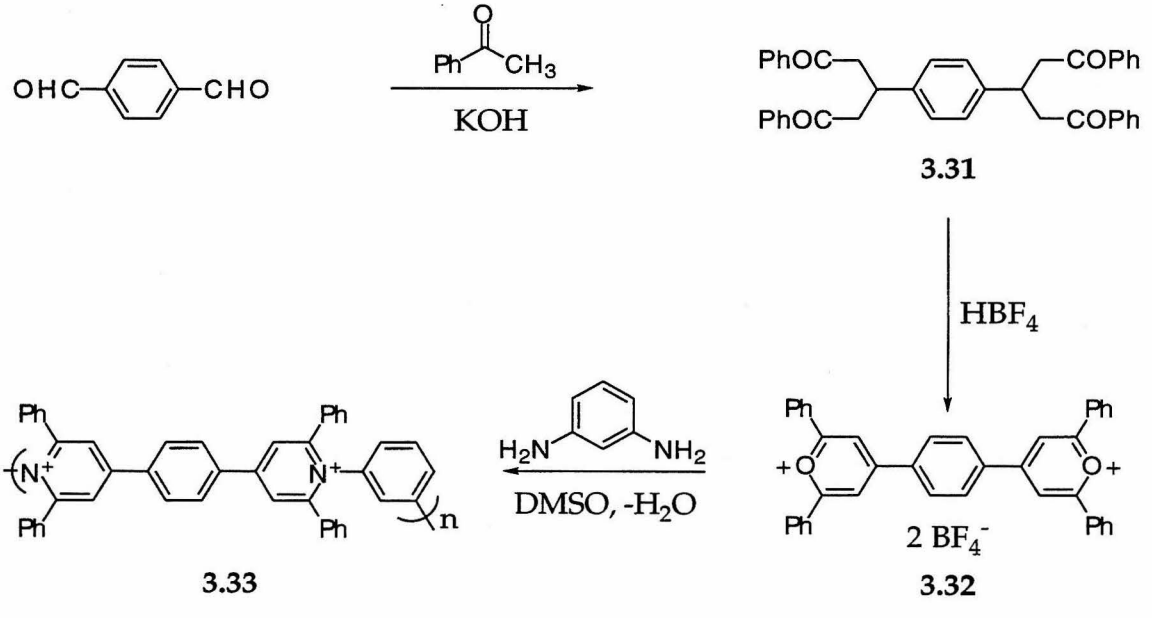
**Conclusions and Future Directions**

It is stressed that these data are preliminary in nature but it is encouraging at least that bipyridiniums may serve as stable spin sources for the polaronic ferromagnet. The observed increase in spin stability of reduced **3.23a** versus diquat may be a consequence of improved steric protection towards

nucleophilic attack or dimerization. More extensive magnetization or EPR studies are required to determine that the diradical dication of **3.23a** is a ground-state triplet. Future directions for diquat systems are unclear, however, as no good synthetic method exists for elaborating small molecule models such as **3.23a** into polymeric analogs.

2,6-Diaryl-bispyrylium salts are highly reactive towards aromatic amines to give *N,N'*-diaryl-bispyridiniums.[34,35] These systems may be polymerized under azeotropic conditions. This avenue has been briefly pursued by the author. Bispyrylium salt **3.32** was synthesized in two steps, and condensed with 1,3-phenylenediamine to yield **3.33** (Scheme **3-14**).

**Scheme 3-14**




No end groups are detectable by $^1$H NMR or IR but an accurate molecular weight could not be determined in DMF by vapor pressure osmometry. Polymer **3.33** forms a tough film upon slow evaporation from DMF but is

insoluble in acetonitrile. Doping studies on this material were not actively pursued. It is expected that the triplet preference will be small in this system because of severe twisting. Unfortunately, unsubstituted pyrylium salts are highly susceptible to hydrolysis and are probably not amenable to this polymerization protocol.

In conclusion, viologens are tentatively proposed as suitable SCs for the polaronic ferromagnet. Their incorporation into a relatively planar polymeric structure, however, has proven to be synthetically unfeasible.

**Experimental Section**

NMR spectra were recorded on a JEOL-GX 400 (399.65 MHz $^{1}H$, 100.4 MHz $^{13}C$) or a GE-300 spectrometer in $CDCl_3$ at room temperature and referenced to residual protons unless specified otherwise. IR spectra were measured on a Perkin-Elmer 1600 instrument in a KBr pellet unless specified otherwise. Melting points were recorded on a Thomas Hoover melting point apparatus and are uncorrected. EI mass spectra , 70 eV, were obtained on a Hewlett-Packard 5890/5970 GC/MS. FAB and exact mass measurements were performed on a ZAB 7070 instrument at the University of California, Riverside. UV/visible spectra were recorded on a Beckman Instruments DU-640 continuous wave spectrometer. Elemental analysis was determined at Atlantic Microlab, Norcross, Georgia and at Caltech.

Electrochemical investigations were performed on a computer controlled potentiostat (EG&G-OAR Versastat). Cyclic voltammmetry experiments employed platinum working and counter electrodes and silver-silver chloride as a pseudoreference electrode. Reduction potentials are referenced to ferrocene/ferroenium ($E^0$ = +0.42 V vs SCE). The working electrode employed for bulk electrolyses was a 10 x 2.5 cm piece of 52 mesh, 99.9% pure platinum gauze shaped into a cylinder. The counter electrode was a 2.5 cm x 2.5 cm piece of 100 mesh, 99.9% pure platinum gauze attached to a platinum wire. A silver-silver chloride isolated in a commercial Vycor-tipped tube served as a pseudo-reference electrode.

**Synthesis**

**3.3.** 1-chloro-2,4-dinitrobenzene (3.092 g, 15.27 mmol), 4, 4'-dipyridyl (2.736 g, 17.5 mmol) and anhydrous methanol (15 ml) were refluxed together under argon. TLC after 4 days indicated that the reaction was almost complete.

Excess 4,4'-dipyridyl (450 mg, 2.87 mmol) was added and the dark reaction mixture refluxed for a further 24 hours. The solution was concentrated to minimum volume and added to diethyl ether. The resulting precipitate was collected by filtration and recrystallized from methanol/diethyl ether to yield 3.65 g (66.6%) of **3.3**. $^{1}H$ NMR ($CD_3OD$): δ 8.15 (d, J = 4.7 Hz, 2 H); 8.38 (d, J = 8.7 Hz, 1 H); 8.83 (d, J = 6.9 Hz, 2 H); 8.90 (d, J = 4.7 Hz, 2 H); 8.95 (dd, J = 2.4, 8.7 Hz, 1 H); 9.30 (d, J = 2.4 Hz, 1 H); 9.45 (d, J = 6.9 Hz, 2 H); $^{13}C$ NMR ($CD_3OD$): δ 123.23; 123.73; 127.07; 131.27; 132.89; 139.86; 142.95; 144.59; 147.79; 151.17; 152.05; 157.99; FAB: 323 ($M^+$, 100); 277 (M-$NO_2$, 6); 231 (M-2$NO_2$, 16); Exact Mass: Calculated for $C_{16}H_{11}N_4O_4$: 323.07803. Found: 323.07670 (-4.1 ppm).

**3.4a.** Compound **3.3a** (810 mg, 2.258 mmol) was suspended in distilled water (20 ml) and the mixture purged with argon. Freshly distilled aniline (0.66 g, 7.13 mmol) was added and the mixture slowly brought to reflux under argon for 12 hours and then allowed to cool to room temperature to yield a brown precipitate of 2,4-dinitroaniline. The filtrate was extracted with diethyl ether. The aqueous extract was concentrated and the resulting yellow solid recrystallized from methanol-acetone to yield 523 mg (86.2%) of pure **3.4a**. $^{1}H$ NMR ($D_2O$): δ 7.77 (m, 5 H); 8.45 (d, J = 5.5 Hz, 2 H); 8.66 (d, J = 6.1 Hz, 2 H); 9.00 (d, J = 5.5 Hz, 2 H); 9.33 (d, J = 6.4 Hz, 2 H); $^{13}C$ NMR ($D_2O$ vs $CD_3OD$): δ 123.73; 124.98; 127.09; 131.73; 132.80; 143.39; 143.53; 145.88; 151.02; 155.43; FAB: 233 ($M^+$, 100); 234 (28); Exact Mass: Calculated for $C_{16}H_{13}N_2$: 233.1079. Found: 233.1075 (-1.7 ppm).

**3.4b.** $^{1}H$ NMR ($CD_3OD$): δ 1.42 (s, 9 H); 7.82 (s, 4 H); 8.10 (d, J = 6.2 Hz, 2H); 8.67 (d, J = 7.0 Hz, 2 H); 8.88 (d, J = 6.2 Hz, 2 H); 9.35 (d, J = 7.0 Hz, 2 H); $^{13}C$ ($CD_3OD$): δ 31.52; 36.01; 123.74; 125.01; 127.22; 128.80; 141.62; 143.65; 146.36; 151.69; 155.56; 156.82; Exact Mass (FAB): Calcd for $C_{20}H_{21}N_2$: 289.1705; Found: 289.1711 (+2.1 ppm).

**3.5a.** 1-chloro-2,4-dinitrobenzene (4.196 g, 20.72 mmol), **3.4a** (944 mg, 3.512 mmol) and anhydrous acetonitrile (30 ml) were combined in a 100 ml flask and the suspension brought to reflux under argon. The reaction's progress was monitored by $^1$H NMR. It appeared to be 70% complete after 6 days. Additional 1-chloro-2,4-dinitrobenzene (3.089 g, 15.2 mmol) was added and reflux continued for a further 24 hours. Acetone (50 ml) was added and the mixture was filtered. Recrystallization from methanol/acetone furnished 758 mg (46%) of pure product. $^1$H NMR ($CD_3OD$): δ 7.81-7.83 (complex multiplet, 3 H); 7.94-7.97 (m, 2 H); 8.42 (d, J = 8.5 Hz, 1 H); 8.97 (m, 3 H); 9.07(d, J = 7.3 Hz, 2 H); 9.33 (d, 2.5 Hz, 1 H); 9.60 (d, J = 7.0 Hz, 2 H); 9.64 (d, J = 7.0 Hz, 2 H); $^{13}$C NMR ($D_2O$ vs $CD_3OD$): δ 123.73; 124.98; 127.09; 131.73; 132.80; 143.39; 143.53; 145.88; 151.02; 155.43; FAB: 233 ($M^+$, 100); 234 (28); Exact Mass: Calculated for $C_{22}H_{16}N_4O_4$: 400.1172. Found: 400.1168 (-1.0 ppm).

**3.5b.** $^1$H NMR ($CD_3OD$): δ 1.44 (s, 9 H); 7.88 (m, 4 H); 8.45 (d, J = 8.7 Hz, 1 H); 8.97 (m, 3 H); 9.08 (d, J = 6.9 Hz, 2 H); 9.32 (d, J = 2.4 Hz, 1 H); 9.58 (d, J = 6.9 Hz, 2 H); 9.65 (d, J = 6.8 Hz, 2 H); $^{13}$C NMR ($CD_3OD$): δ 31.51; 36.08; 123.15; 125.16; 128.43; 128.73; 128.90; 131.31; 132.86; 139.79; 141.63; 144.52; 147.02; 148.48; 151.16; 151.34; 154.00; 157.23; Exact Mass: Calcd for $C_{26}H_{24}N_4O_4$: 456.1798; Found: 456.1817 (+4.2 ppm).

**2,4 bispyridyl-pyrimidinium dichloride (3.11).** 2,4-Dichloropyrimidine (655.7 mg, 4.401 mmol) was dissolved in dry acetonitrile (16 ml) in a 50 ml three-necked flask. Anhydrous pyridine (0.73 g, 9.3 mmol) was added and the solution brought to reflux under argon. The solution gradually turned yellow and formed a white precipitate. Reflux was continued for 12 hours, the reaction mixture was then cooled and the precipitate collected by filtration and recrystallized from water-acetone to yield 762 mg (56.4%) of pure product. $^1$H NMR ($D_2O$): δ 8.42-8.48 (m, β2 β4, 4 H); 8.65 (d, J = 6.8 Hz, $H_5$); 8.95-9.04 (m,

γ2 γ3, 2 H); 9.61 (d, J = 6.8 Hz, $H_6$); 9.80 (d, J = 6.6 Hz, α4); 10.19 (d, J = 6.8 Hz, α2, 2 H).

Product was dissolved in a minimum amount of water and added to a concentrated solution of ammonium hexafluorophosphate yielding a white precipitate which was recrystallized from acetonitrile-diethyl ether.

$^1$H NMR (dmso-$d_6$): δ 8.45-8.56 (m, β2 β4, 4 H); 8.87 (d, J = 5.5 Hz, $H_5$); 9.01-9.08 (m, γ2 γ3, 2 H); 9.79 (d, J = 5.5 Hz, $H_6$); 10.07 (d, J = 6.0 Hz, α4); 10.28 (d, J = 6.0 Hz, α2, 2 H); $^{13}$C NMR ($CD_3CN$): δ 116.44; 117.18; 128.38; 128.69; 141.06; 142.35; 151.38; 151.61; 159.73; 165.28.

**2,4,6-Trifluoropyrimidine.** 2,4,6-Trichloropyrimidine (6.28 g, 0.0342 mol), biscyclohexanato-18-crown-6 (20 mg), anhydrous potassium fluoride (17.70 g, 0.3046 mol) and dry tetraglyme (30 ml) were combined together in a 100 ml three-necked flask fitted with a magnetic stirrer. The suspension was warmed to 150°C under argon. GC/MS after six hours indicated that starting material was remaining so a further portion of potassium fluoride (6.0 g, 0.10 mol) was added and stirring continued for a further six hours. The reaction mixture was cooled and distillation through a simple condenser yielded 550 mg (12%) of desired product contaminated with ca. 1% of tetraglyme (by $^1$H NMR); $^1$H NMR ($CDCl_3$): δ 6.56 (s, 1 H).

**2,4 Dibromopyrimidine (3.14).** 2,4-Dichloropyrimidine (0.999 g, 6.70 mmol) and phosphorous tribromide (34.2 g, 0.126 mol) were heated together at 175°C for six hours, cooled to room temperature, and then carefully added to ice. GC/MS indicated that the reaction was 80% complete. A further quantity of phosphorous tribromide (14.3 g, 0.053 mol) was added and the mixture heated to 175°C for a further five hours, cooled and added to ice. Diethyl ether was added and the layers were separated. The organic layer was dried over $MgSO_4$ and concentrated to yield 1.065 g (66.8%) of desired product. $^1$H NMR ($CDCl_3$):

δ 7.51 (d, J = 5.2 Hz, 1 H); 8.32 (d, J = 5.2 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$): δ 124.64; 151.96; 153.36; 159.03; GC/MS: 240 ($M^+$, $2^{81}Br$, 48); 238 ($M^+$, $^{81}Br^{79}Br$, 100); 236 ($M^+$, $2^{79}Br$, 50); 159(90); 157 (93).

**2,4-Diiodopyrimidine (3.15).** 2,4-Dichloropyrimidine (0.850 g, 5.71 mmol) was stirred in 47% hydriodic acid (4 ml) for 24 hours. Water (20 ml) was added and the resulting precipitate was collected by filtration. The red filter cake was dissolved in diethyl ether, washed with an aqueous sodium thiosulfate solution to remove excess iodine and concentrated under vacuum to yield a white solid. Subsequent recrystallization from hexanes yielded 538 mg (28.4%) of pure 2,4-diiodopyrimidine as white needles which darken upon exposure to light; $^1H$ NMR ($CDCl_3$): δ 7.75 (d, J = 5.1 Hz, 1 H); 7.96 (d, J = 5.1 Hz, 1 H).

**5-Bromo-2-methylsulfenylpyridine (3.17).** 2,5-Dibomopyridine (30.72 g, 0.1296 mol), anhydrous benzene (90 ml), sodium methanethiolate (15% in $H_2O$, 85 ml, 0.196 mol) and tetrabutylammonium bromide (1.50 g, 4.66 mmol) were refluxed together under argon. Extent of reaction was monitored by GC/MS and the reaction was 90% complete after 2 days. A further 30 ml of aqueous sodium methanethiolate was added and reflux continued for a further 36 hours and then the reaction mixture was cooled to room temperature and placed in an extraction funnel. The benzene layer was separated and the aqueous layer washed with methylene chloride (3 x 60 ml). Combined organic layers were washed with saturated NaCl and dried over $MgSO_4$. Sublimation under vacuum (50°C/500 mtorr) afforded25.43 g (96%) of pure product as white crystals. $^1H$ NMR ($CDCl_3$): δ 2.54 (s, 3 H); 7.08 (d, J = 8.6 Hz, 1 H); 7.58 (dd, J = 2.2 Hz, 8.6 Hz, 2 H); 8.49 (d, J = 2.2 Hz, 1 H); GC/MS: 203($M^+$,69); 205($M^+$,67); 159(33); 157(32); 78(100).

**5-Bromo-2-methylsulfinylpyridine (3.18).** **3.17** (15.934 g, 0.0781 mol) and

glacial acetic acid (45 ml) were stirred together and cooled to 0°C. Aqueous hydrogen peroxide (10.0 ml, 30% w/w) was added dropwise via syringe. The solution was stirred at room temperature under argon for 36 hours, added to methylene chloride (100 ml) and neutralized with aqueous $Na_2CO_3$. The layers were separated and the aqueous layer was washed with further quantities of methylene chloride. The organic layer was dried over $MgSO_4$ and concentrated. The residue was recrystallized from cyclohexane to yield 14.417 g (78%) of desired product. mp 65-66°C; $^1$H NMR ($CDCl_3$): δ 2.85 (s, 3 H); 7.94 (d, J = 8.3 Hz, 1 H); 8.09 (m, 1 H); 8.68 (d, J = 2.5 Hz, 1 H); GC/MS: 221($M^+$,35); 219($M^+$,32); 204(24); 202(16); 173(100); 158(80); 76(94).

**5,5'-Dibromo-2,2'-bipyridine (3.19).** Compound **3.18** (24.19 g, 0.1099 mol) was dissolved in dry THF (250 ml) and the solution cooled to -35°C. A solution of ethylmagnesium bromide in THF (76 ml, 1.0 M, 76 mmol) was added dropwise via syringe and the resultant dark brown mixture was slowly warmed to room temperature and stirred overnight. The mixture was then cautiously poured onto 100 g of crushed ice, neutralized with 1 M HCl solution and the solution's pH adjusted to 9 with $Na_2CO_3$. The precipitate was collected on a frit, added to chloroform (200 ml) and hot-gravity filtered. The organic layer was concentrated, and the residue recrystallized from 1:1 chloroform/ethanol to yield 8.45 g (49%) of desired product as pale plates. $^1$H NMR ($CDCl_3$): δ 7.93 (dd, J = 8.5, 2.2 Hz, 2 H); 8.29 (d, J = 8.5 Hz, 2 H); 8.71 (d, J = 2.2 Hz, 2 H).

**5-Bromo-5'-trimethylsilyl-2,2'-bipyridine (3.20).** In a thick-walled Schlenk flask fitted with a magnetic stirbar were combined **3.19** (4.452 g, 14.17 mmol), hexamethyldisilane (0.72 g, 4.9 mmol), $Pd(PPh_3)_4$ (250 mg, 3%) and freshly distilled HMPA (28 ml). The mixture was degassed by several freeze-pump-thaw cycles and the flask was then sealed. The reaction mixture was then

warmed to 125°C whereupon a yellow solution formed and further heated to 150-160°C for 4 days. It was then cooled to room temperature, added to diethyl ether (50 ml) and precipitated unreacted dibromide was recovered. The filtrate was concentrated and chromatographed on silica gel using chloroform as eluant afforded 801 mg (88%) of pure product. mp 75°C; $^1$H NMR ($CDCl_3$): δ 0.34 (s, 9 H); 7.91-7.96 (m, 2 H); 8.31 (d, J = 2.0 Hz, 1 H); 8.34 (d, J = 2.9 Hz, 1 H); 8.72 (d, J = 2.0 Hz, 1 H); 8.74 (s, 1 H); $^{13}$C ($CDCl_3$): δ -1.33; 120.11; 121.10; 122.29; 135.74; 139.44; 142.15; 150.21; 153.40; 154.80; 155.17; GC/MS 308($M^+$,27); 306($M^+$,25); 293(100).

**5,5'-Dibromo-6,7-dihydropyrido-[1,2-*a*:2,1'-*c*]-pyrazinediium dibromide (3.21).** Dibromide **3.19** (830 mg, 2.64 mmol) and dibromoethane (7 ml) were refluxed together for 7 days, cooled and filtered. Considerable amounts of starting material were still present in the filtrate. The mother liquor was added to nitrobenzene (8 ml) and reflux was continued for a further 6 days. The reaction mixture was then cooled and filtered. The filter cake was redissolved in water and extracted with chloroform. The aqueous layer was lyophilized and purified by column chromatography (3:1, MeOH/2 N $NH_4Cl$). The desired fraction was collected and lyophilized. It was then redissolved in a minimum amount of water and a saturated solution of $NH_4PF_6$ was added. The precipitate was collected and washed well with water to yield 713 mg (63%) of desired product as the hexafluorophosphate salt. $^1$H NMR (acetone-$d_6$): δ 5.68 (s, 4 H); 9.16 (d, J = 8.7 Hz, 2 H); 9.31 (dd, J = 1.9, 8.7 Hz, 2 H); 9.84 (s, 2 H).

**3, 5-Dibromo-*tert*-butyl benzene (3.24).**[36] *tert*-Butyl aniline (10.03 g, 67.21 mmol), concentrated hydrochloric acid (6.4 ml) and water (250 ml) were combined in a 500 ml three-necked flask fitted with a mechanical stirrer. Bromine (35 g, 0.22 mol) suspended in water (100 ml) was added in small

portions over thirty-five minutes yielding a white suspension and a reddish oil. The mixture was stirred for 1 hour, solid sodium thiosulfate and sodium bicarbonate were then successively added and the mixture extracted with diethyl ether and concentrated. The residue was then dissolved in methylene chloride and passed through a short column of silica gel to yield the desired product as a red oil sufficiently pure to be carried on to the next step.

GC/MS: 309 ($M^+$, $2^{81}Br$, 12); 307 ($M^+$, $^{81}Br^{79}Br$, 24); 305 ($M^+$, $2^{79}Br$, 12); 294 (M-$CH_3$, 49); 292 (100); 290 (48).

To a stirring solution of *tert*-butyl nitrite (7.5 g, 0.073 mol) in DMF (100 ml) was added a solution of crude amine over 20 minutes (14.95 g, 48.7 mmol) in reagent grade DMF (40 ml) at 50°C. The mixture was stirred at this temperature for 30 minutes, cooled to room temperature and partitioned between diethyl ether and water. The organic extract was concentrated and chromatographed on silica gel using hexanes as eluant. The highest running fraction was collected and distilled at 130°C-1.5 torr to yield 9.51 g (67%), 57% overall, of pure product as a clear oil; $^1H$ NMR ($CDCl_3$): δ 1.29 (s, 9 H); 7.43 (d, J = 1.6 Hz, 2 H); 7.48 (t, J = 1.6 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$): δ 31.02; 35.09; 122.70; 121.56; 127.57; 131.09; 155.27.

**3, 5 Bis(trimethylsilyl)*tert*-butyl benzene (3.25).** To a mixture of magnesium turnings (0.939 g, 38.6 mmol) in anhydrous THF (10 ml) was added dropwise a solution of bisbromide (4.91 g, 16.8 mmol) in 20 ml of dry THF. The reaction was initiated by the addition of iodine crystals and the reaction mixture brought to reflux for 1 hour before dry trimethylsilyl chloride (4.28 g, 39.2 mmol) was added in small portions. The solution was then refluxed overnight and the resulting yellow suspension cooled and added to a saturated $NH_4Cl$ solution. The biphasic mixture was then partitioned between hexanes and water. The organic layer was concentrated and passed

through a short column of silica gel using hexanes as eluant to yield 3.96 g (72%) of a clear oil, shown to be a mixture of 28% monofunctionalized and 72% desired product. Product purity may be raised to > 90% by fractional distillation at 56°C/0.08 torr. GC/MS: 278 ($M^+$,11); 263 (M-$CH_3$,100); 73 ($C_3H_9Si$,15).

**5-*tert*-Butylbenzene-1,3-bis-(1,3,2-benzodioxaborole) (3.26).** Crude bistrimethylsilyl benzene **3.25** (3.347 g, 9.04 mmol) was dissolved in anhydrous methylene chloride (45 ml) and cooled to -78°C in a dry-ice bath. A solution of $BBr_3$ in methylene chloride (1.0 M, 26 ml, 26 mmol) was cautiously added. The mixture was stirred for 1 hour at this temperature, warmed to room temperature and then refluxed under argon for 12 hours. The solution was then cooled to 0°C and catechol (2.880 g, 21.6 mmol) was added in one portion and stirred at room temperature for 9 hours. The solvent was then evaporated and the resulting brown solid washed well with acetone yielding 1.265 g (20.3%) of a white solid. mp 231-234°C; $^1H$ NMR ($CDCl_3$): δ 1.46 (s, 9 H); 7.14-7.18 (dd, J = 3.3, 5.8 Hz, 4 H); 7.34-7.37 (dd, J = 3.3, 5.8 Hz, 4 H); 8.33 (s, 2 H); 8.67 (s, 1 H); $^{13}C$ NMR ($CDCl_3$): δ 31.35; 34.86;112.57; 122.80; 125.47 (br, C-B); 135.68; 148.49; 150.59; DCI/$NH_3$: 370 ($M^+$, 89); 355 (M-15, 100); 135 (51).

**3.27.** 4-*tert*-Butyl benzeneboronic acid (711 mg, 4.00 mmol), dibromide **3.19** (1.420 g, 4.52 mmol), $Pd(PPh_3)_4$ (15 mg, 3%) and toluene (15 ml) were combined in a 25 ml three-necked flask and the mixture purged with argon. Aqueous $Na_2CO_3$ (2 M, 4 ml) was added and the mixture brought to reflux under argon. Reflux was continued overnight and the reaction mixture was cooled. Methylene chloride was added and the layers separated. Column chromatography on silica gel (5-15% EtOAc/petroleum ether) furnished 766 mg (52%) of desired product and an additional 280 mg (17%) of bisubstituted

material. mp 180-182°C; $^1$H NMR ($CDCl_3$): δ 0.36 (s, 18 H); 1.47 (s, 9 H); 7.71 (s, 3 H); 7.96 (dd, J = 1.5, 7.8 Hz, 2 H); 8.09 (dd, J = 2.2, 8.2 Hz, 2 H); 8.42 (d, J = 7.8 Hz, 2 H); 8.53 (d, J = 8.2 Hz, 2 H); 8.80 (s, 2 H); 8.99 (s, 2 H); $^{13}$C ($CDCl_3$): δ -1.32; 31.39; 35.08; 120.23; 120.94; 124.13; 135.30; 135.37; 136.67; 138.42; 142.09; 147.81; 153.05; 153.40; 155.26; 155.81

**Compound 3.28**. Bisboronic ester **3.26** (61.5 mg, 0.1662 mmol), **3.20** (102.1 mg, 0.3323 mmol) and $Pd(PPh_3)_4$ (10 mg, 3%) dissolved in toluene (7 ml) and the mixture purged with argon. An argon-purged aqueous $Na_2CO_3$ solution (2 M, 2 ml) was added and the mixture brought to reflux under argon. A dark solid precipitated after approximately 20 minutes and the color of the organic layer was discharged. Reflux was continued for 24 hours; the reaction mixture was then allowed cool and the organic layer was extracted with diethyl ether (40 ml), washed with water and dried over $MgSO_4$. Column chromatography over silica gel (15% ethyl acetate/petroleum ether) furnished 56 mg (57%) of pure **3.28a**. $^1$H NMR ($CDCl_3$): δ 0.36 (s, 18 H); 1.47 (s, 9 H); 7.71 (s, 3 H); 7.96 (dd, J = 1.5, 7.8 Hz, 2 H); 8.09 (dd, J = 2.2, 8.2 Hz, 2 H); 8.42 (d, J = 7.8 Hz, 2 H); 8.53 (d, J = 8.2 Hz, 2 H); 8.80 (s, 2 H); 8.99 (s, 2 H); $^{13}$C ($CDCl_3$): δ -1.32; 31.39; 35.08; 120.23; 120.94; 124.13; 135.30; 135.37; 136.67; 138.42; 142.09; 147.81; 153.05; 153.40; 155.26; 155.81; Exact Mass (FAB): Calcd. for $C_{36}H_{42}N_4Si_2$: 586.2948; Found: 586.2963 (+2.5 ppm).

**Compound 3.23a**. **3.28a** (139 mg, 0.237 mmol) and dibromoethane (5 ml) were refluxed together for 24 hours. A yellow precipitate formed and the characteristic solution-phase fluorescence of bipyridine disappeared indicating complete consumption of starting material. 2-Ethoxyethanol (10 ml) was added and reflux continued for 15 days. The solvent was then removed under high vacuum, the residue was redissolved in methanol and product was precipitated with diethyl ether and dried under vacuum to yield 187 mg

(98%) of tetrabromide salt. Dissolution in a minimum amount of methanol and addition of aqueous $NH_4PF_6$ afforded the $PF_6^-$ salt. $^1H$ NMR ($CD_3OD$): δ 0.53 (s, 18 H); 1.56 (s, 9 H); 5.47 (m, 4 H); 5.58 (m, 4 H); 8.33 (s, 2 H); 8.70 (s, 1 H); 9.04 (m, 4 H); 9.20 (d, J = 8.6 Hz, 2 H); 9.34 (s, 2 H); 9.45 (dd, J = 8.6, 1.4 Hz, 2 H); 10.15 (s, 2 H). $^1H$ NMR (acetone-$d_6$, $PF_6^-$): δ 0.51 (s, 18 H); 1.47 (s, 9 H); 5.68 (s, 8 H); 8.35 (s, 2 H); 8.46 (s, 1H); 9.20-9.40 (m, 6 H); 9.47 (m, 2 H); 9.53 (s, 2 H); 9.94 (s, 2 H); $^{13}C$ (acetone-$d_6$, $PF_6^-$): δ -1.97; 31.37; 36.27; 53.51; 54.30; 125.68; 127.99; 128.63; 129.31; 135.05; 139.84; 140.64; 143.19; 146.20; 146.75; 147.04; 151.66; 153.76; 156.08; Exact Mass (FAB): $M^+$ not observed but 1077 (M + 3 $PF_6^-$), 932 (M + 2 $PF_6^-$), 787 (M + $PF_6^-$) and 614 (M-$C_2H_4$) found. Calcd. for $C_{40}H_{50}N_4Si_2$ (+3 $PF_6^-$): 1077.2500; Found: 1077.2484 (-1.4 ppm).

**3.29.** Benzeneboronic acid (48 mg, 0.39 mmol), **3.20** (54 mg, 0.176 mmol), toluene (8 ml) and $Pd(PPh_3)_4$ (5 mg, 3%) were combined in a 25 ml three-necked flask and the solution was purged with argon. Aqueous $Na_2CO_3$ (4 ml, 8 mmol) was added and the mixture refluxed under argon for 24 hours. The layers were separated and column chromatography on silica gel (5-25% EtOAc/petroleum ether) afforded 52 mg (97%) of pure X. mp 97-98°C; $^1H$ NMR ($CDCl_3$): δ 0.35 (s, 9 H); 7.41-7.52 (m, 3 H); 7.64-7.67 (m, 2 H); 7.94 (dd, J = 1.7, 7.8 Hz, 1 H); 8.02 (dd, J = 2.2, 8.2 Hz, 1 H); 8.39 (d, J = 7.8 Hz, 1 H); 8.49 (d, J = 8.2 Hz, 1 H); 8.78 (s, 1 H); 8.93 (s, 1 H); $^{13}C$ NMR ($CDCl_3$): δ -1.30; 120.20; 120.94; 127.05; 128.15; 129.09; 135.19; 135.25; 136.46; 137.61; 142.10; 147.64; 153.40; 155.04; 155.84; GC/MS: 304($M^+$,44); 289(100); 145(9).

**3.30.** Compound **3.29** (49 mg, 0.16 mmol) and dibromoethane (6 ml) were refluxed together for 24 hours. Water (20 ml) and methanol (2 ml) were added and the layers separated. The aqueous layer was lyophilized to yield 69 mg (88%) of pure **3.30** as a yellow powder. $^1H$ NMR ($CD_3OD$): δ 0.52 (s, 9 H); 5.42 (s, 4 H); 7.67 (m, 3 H); 8.02 (m, 2 H); 9.02 (s, 2 H); 9.12 (m, 1 H); 9.19 (m, 1

H); 9.31 (s, 1 H); 9.74 (s, 1 H).

$^1$H NMR (acetone-$d_6$): δ 0.50 (s, 9 H); 5.70 (s, 4 H); 7.68 (s, 3 H); 8.04 (s, 2 H); 8.09 (dd, J = 2.2, 8.2 Hz, 2 H); 9.19 (s, 2 H); 9.90 (s, 2 H); 8.80 (s, 2 H); 9.50 (s, 1 H); (9.89 s, 1 H); (4 $Br^-$) $^1$H NMR ($CD_3OD$): δ 0.52 (s, 9 H); 5.42 (s, 4 H); 7.67 (m, 3 H); 8.01 (m, 2 H); 9.02 (s, 2 H); 9.12 (s, 2 H); 9.31 (s, 1 H); 9.74 (s, 1 H).

**3.31.** Terephthaldehyde (5.50 g, 0.0410 mol), acetophenone (28.8 g, 0.240 mol) and absolute ethanol (300 ml) were combined together in a 500 ml flask. A solution of potassium hydroxide (3 g, 0.05 mol) in water (12 ml) was slowly added over thirty minutes forming a pink precipitate. The reaction mixture was refluxed under argon overnight, cooled to room temperature and washed well with water to remove excess base to furnish 13.10 g (55%) of crude (97% pure by NMR) product. Recrystallization from chloroform/hexanes affords analytically pure product; mp 204-205°C; $^1$H NMR ($CD_2Cl_2$): δ 3.36 (m, 8 H); 3.99 (quintet, J = 6.8 Hz, 2 H); 7.21 (s, 4 H); 7.44 (m, 8 H); 7.54 (m, 4 H); 7.91 (d, J = 8.3 Hz, 8 H); EI/FAB: 579 ($M^+$, 6); 459 (48); 339 (50); Exact Mass Calcd: 579.2535; Found: 579.2554 (+3.3 ppm).

**3.32.** Triphenylmethanol (0.997 g, 3.83 mmol) and acetic anhydride (20 ml) were combined in a 50 ml three-necked flask. To the pale yellow solution was added 48% fluoboric acid (0.30 ml, 0.42 g, 2.3 mmol) dropwise with ice cooling. A deep red solution was formed which was stirred for two hours at room temperature. Tetraketone **3.31** (0.996 g, 1.72 mmol) was added in one portion and the mixture brought to reflux under nitrogen for one hour and cooled. The yellow precipitate was collected by filtration, washed with additional acetic anhydride, acetone and dried under vacuum to yield 880 mg (72%) of desired product. mp >350°C; $^1$H NMR (dmso-$d_6$); δ 9.24 (s, 4 H); 7.1-8.9 (m, 20 H); Exact Mass Calcd for $C_{40}H_{28}O_2$: 540.2089; Found: 540.2079 (-1.9 ppm).

**3.33.** Bispyrylium salt **3.32** (725 mg, 1.015 mmol) and 1,3-phenylenediamine

(112 mg, 1.036 mmol) were combined in a 25 ml Schlenk flask. DMSO (8 ml) was added and the mixture warmed to 150°C under argon. Toluene (10 ml) was added and the toluene/water azeotrope removed overnight. Stirring was then continued for a further 12 hours at 150°C and the dark solution was added to diethyl ether (200 ml). The green precipitate was redissolved in DMF and precipitated in diethyl ether. Final drying at 90°C afforded 420 mg (58%) of polymer. $^1$H NMR (dmso-$d_6$); δ 6.9-8.0 (m, 24 H); 8.4-8.8 (m, 4 H); Calcd for $C_{46}H_{32}N_2B_2F_8$: C: 70.26; H: 4.10; N: 3.56. Found: C: 67.62; H: 4.66; N: 3.69.

**References**

(1) Hünig, S.; Berneth, H. *T. Curr. Chem.* **1980**, *92*, 1.

(2) Bird, C. L.; Kuhn, A. T. *Chem. Soc. Rev.* **1981**, *10*, 49.

(3) Nagamura, T.; Isoda, Y.; Sakai, K. *Polym. Int.* **1992**, *27*, 125.

(4) Murray, M. M.; Kaszynski, P.; Kaisaki, D. A.; Chang, W.; Dougherty, D. A. *J. Am. Chem. Soc.* **1994**, *116*, 8152-8161.

(5) Hünig, S.; Schenk, W. *Liebegs. Ann. Chem.* **1979**, 1523.

(6) Kamogawa, H.; Satoh, S. *J. Poly. Sci. Part A: Poly. Chem.* **1988**, *26*, 653.

(7) Marvell, E. N.; Caple, G.; Shahidi, I. *J. Amer. Chem. Soc.* **1970**, *92*, 5641.

(8) Marvell, E. N.; Caple, G.; Shahidi, I. *J. Amer. Chem. Soc.* **1970**, *92*, 5646.

(9) McArdle, C. B. *Applied Photochromic Polymer Systems*; Chapman and Hill: New York, NY, 1992, pp 206-255.

(10) Allen, J. G. *Br. Patent 1 399 595* **1975**.

(11) Murakami, M.; Hajima, M.; Takami, F.; Yoshioka *Heterocycles* **1990**, *31*, 2055.

(12) Skalski, B.; Wenska, G.; Gdaniec, Z.; Adamiak, R. W. *Tetrahedron* **1993**, *49*, 5859.

(13) Svirskaya, P. I.; Yedidia, V.; Leznoff, C. C.; Miller, J. M. *J. Heterocyclic Chem.* **1985**, *22*, 149.

(14) Caton, M. P. L.; Hurst, D. T.; McOmie, J. F. W.; Hunt, R. R. *J. Chem. Soc. (C)* **1967**, 1204.

(15) Edo, K.; Sakamoto, T.; Yamanaka, H. *Chem. Pharm. Bull.* **1978**, *26*, 3843.

(16) Weiss, R.; Pomrehn, B.; Hampel, F.; Bauer, W. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1319.

(17) Sullivan, P. D.; Williams, M. L. *J. Amer. Chem. Soc.* **1976**, *98*, 1711.

(18) Sanchez-Palacios, A.; Delgado, R. *Appl. Spect.* **1994**, *48*, 926.

(19) Rieger, A. L.; Rieger, P. H. *J. Phys. Chem.* **1984**, *88*, 5845.

(20) Yamamoto, T.; Maruyama, T.; Zhou, Z.; Ito, T.; Fukuda, T.; Yoneda, Y.; Begum, F.; Ikeda, T.; Sasaki, S.; Takezoe, H.; Fukuda, A.; Kubota, K. *J. Amer. Chem. Soc.* **1994**, *116*, 4832.

(21) Oae, S.; Kawai, T.; Furukawa, N. *Phosphorus and Sulfur* **1987**, *34*, 123.

(22) Evans, A. G.; Evans, J. C.; Baker, M. W. *J. Amer. Chem. Soc.* **1977**, *99*, 5882.

(23) Babin, P.; Bennetau, B.; Theurig, M.; Dunogués, J. *J. Organomet. Chem.* **1993**, *446*, 135.

(24) Zoltewicz, J. A.; Cruskie, M. P.; Dill, C. D. *J. Org. Chem.* **1995**, *60*, 264.

(25) Norris, D. J.; Bunting, J. W.; Meathrel, W. G. *Can. J. Chem.* **1977**, *55*, 2601.

(26) Thompson, W. J.; Gaudino, J. *J. Org. Chem.* **1984**, *49*, 5237.

(27) Wright, S. W.; Hageman, D. L.; McClure, L. D. *J. Org. Chem.* **1994**, *59*, 6095.

(28) Zoltewicz, J. A.; Cruskie, M. P. *J. Org. Chem.* **1995**, *60*, 3487.

(29) Stille, J. K. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508.

(30) Mitchell, T. M. *Synthesis* **1992**, 803.

(31) See Chapter 2 of this dissertation.

(32) Monk, P. M. S.; Fairweather, R. D.; Ingram, M. D.; Duffy, J. A. *J. Chem. Soc. Perkin Trans. 2* **1992**, 2039.

(33) Pirzada, N. H.; Pojer, P. M.; Summers, L. A. *Z. Naturforsch.* **1976**, *31b*, 115.

(34) Harris, F. W.; Chuang, K. C.; Huang, S. A. X.; Janimak, J. J. *Polymer* **1994**, *35*, 4940.

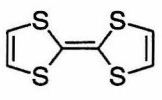
(35) Katritzky, A. R.; Tarr, R. D.; Heilmann, S. M.; Rasmussen, J. K.; Krepski, L. R. *J. Polymer Science: PartA: Polymer Chemistry* **1988**, *26*, 3323.

(36) Iwamura, H.; Ishida, T. *J. Amer. Chem. Soc.* **1991**, *113*, 4238.

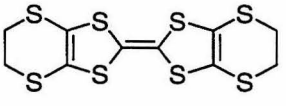
# Appendix A.

## Synthetic Efforts Towards Soluble Poly(*meta*-Tetrathiafulvalene)

Tetrathiafulvalene (TTF, **A.1**) has been the subject of intense research activity by chemists and physicists alike since the discovery of high electrical conductivity in its charge-transfer complex with tetracyanoquinodimethane (TCNQ) in the early 1970's.[1-3] The complex is considered to be the first example of an "organic metal"–its conductivity rises upon lowering temperature. The β phase of $(BEDT\text{-}TTF)_2 I_3$ (**A.2**), a close relative of TTF, becomes superconductive at 1.4 K under ambient pressure. Several TTF derivatives have since been prepared and many show superior properties to the parent molecule. Technological implications aside, this class of materials offers a wealth of information about close range electronic interactions in the solid state.



**A.1**

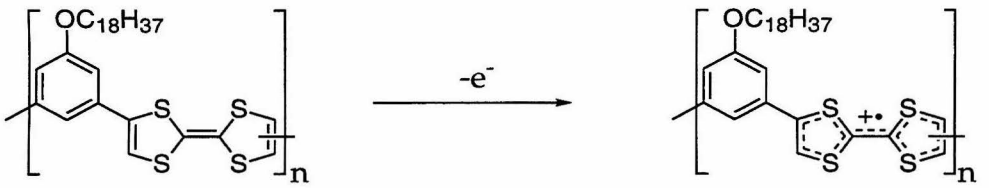


**A.2**

The electrochemical behavior of TTF is well documented: the material has two separate reversible redox waves at 0.39 V and 0.62 V versus SCE[4] and is readily oxidized by iodine. The radical cation is very stable; a water-soluble TTF derivative forms a conductive π-stack upon preparative one-electron oxidation.[5] As such, it represents an interesting SC unit for the polaronic ferromagnet model described in Chapter 2. The corresponding polymer (**A.3**) has potentially interesting magnetic and electrical properties when doped with a suitable oxidant.

Early work in this group established that unsubstituted poly(*meta*-TTF) is insoluble in organic solvents.[6] An attempt was made, therefore, to incorporate an octadecyl sidechain in the 5-position in the hope of improving

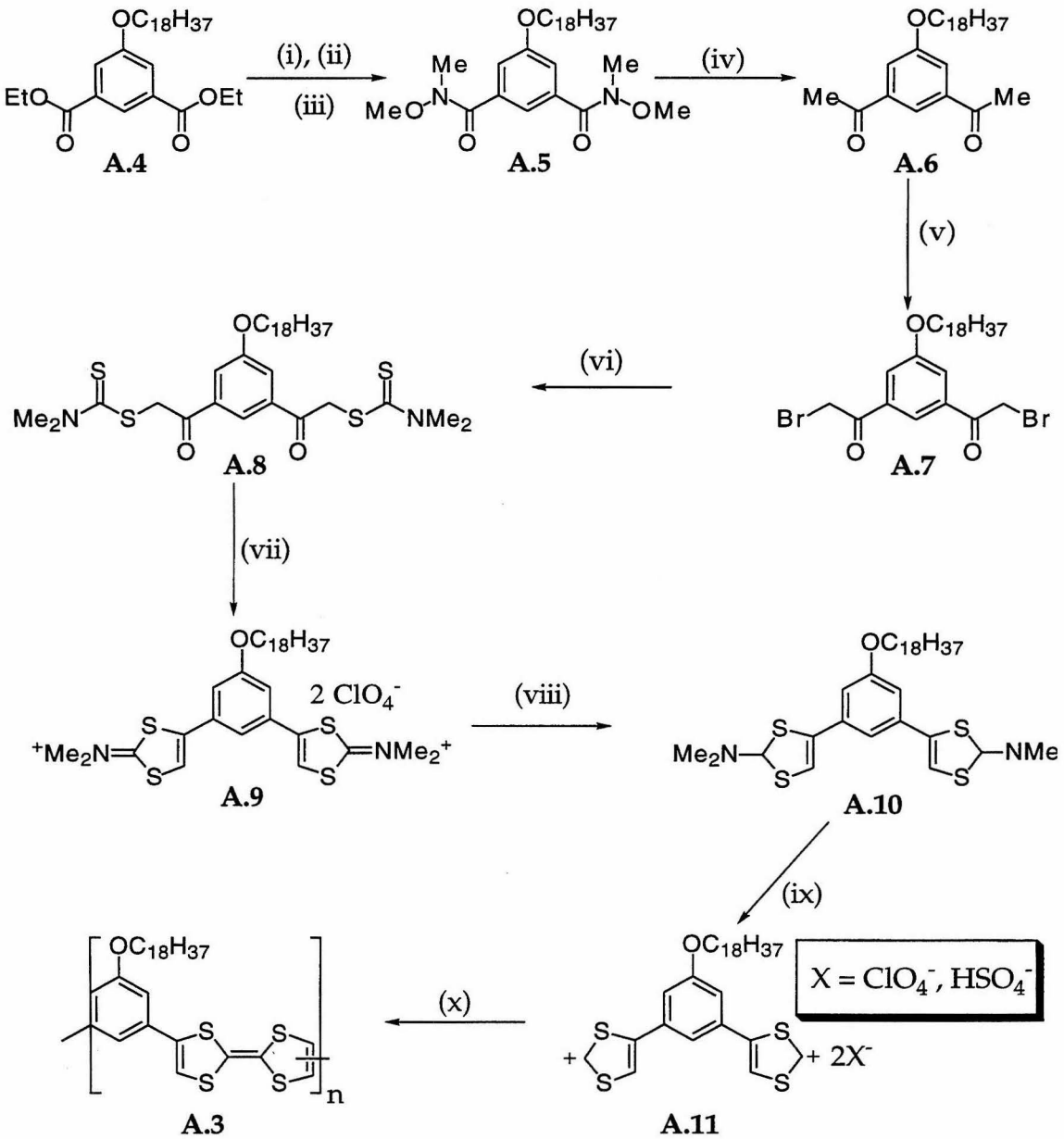
solubility.



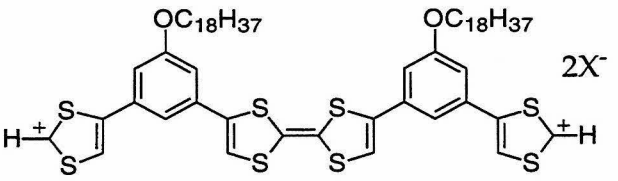

**A.3**

An eight-step sequence was devised starting from diester **A.4** and is outlined in Scheme A-1. The synthesis of **A.4** has already been described in chapter 2 of this dissertation. Conversion to the Weinreb amides and reduction with methyl lithium affords diketone **A.6** in high yield. This may be brominated regioselectively in chloroform to yield bis(acetyl bromide) **A.7**. Subsequent treatment with the sodium salt of *N,N'* Dimethyldithiocarbamic acid and ring closure in perchloric acid[7] afforded bis(immonium dithiole) salt **A.9**. Starting material was recovered using reported procedure employing a fluoboric acid/acetic acid mixture to bring about ring closure.[8] Reduction with sodium borohydride and treatment with mineral acid afforded **A.11**. Sulfuric acid yields relatively pure material as determined by $^1$H NMR. Addition of either perchloric acid or tetrafluoroboric acid to **A.10**, however, forms a significant amount of red material believed to be dimeric **A.12** as determined by NMR and UV spectroscopy. Presumably, the desired dithiolium salt is in equilibrium with free carbene under these conditions. In any event, treatment of either the sulfate or perchlorate salts of **A.11** with triethylamine in acetone resulted in immediate precipitation of a red solid, completely insoluble in all organic solvents.

**Scheme A-1**




**Legend.** (i) KOH; (ii) ClCOCOCl, $CH_2Cl_2$; (iii) MeNHOMe.HCl; (iv) MeLi; (v) $Br_2$, $CHCl_3$; (vi) $NaSCSNMe_2$; (vii) $HClO_4$, Δ; (viii) $NaBH_4$, EtOH; (ix) HX, $Ac_2O$; (x) $Et_3N$, acetone.




**A.12** $X = ClO_4^-, BF_4^-$

**Outlook and Discussion**

The failure of this project demonstrates that long alkyl chains have limitations in solubilizing polymers in organic solvents. The key polymerization step in Scheme A-1 is conducted in polar solvents such as acetone or pyridine.[9] It is unclear if low solubility is a function of polar end groups or $\pi$-stacking of the neutral polymer. It may be possible to synthesize this material by a Stille coupling; monostannylated TTF derivatives are known to undergo cross-coupling in good yield.[10]

Recent theoretical[11] and experimental evidence,[4,12] however, suggests that spin density of TTF's radical cation is located primarily on carbons forming the central double bond. Presumably, spin at these positions is stabilized because of two adjacent sulfur atoms versus one adjacent sulfur for peripheral carbons. The high-spin preference in the polaronic ferromagnet may be weak as a result.

**Experimental**

**A.5** Diester **A.4** (10.17 g, 0.0220 mol), potassium hydroxide (3.8 g, 0.068 mol) and reagent grade methanol (200 ml) were refluxed together under argon for 4 hours and cooled, yielding a yellow solution. Solvent was removed by rotoevaporation and the resulting yellow solid placed under high vacuum overnight. The residue was added to dry benzene (100 ml) and oxalyl chloride (10.91 g, 0.086 mol) was slowly added with stirring, a vigorous reaction ensued yielding copious amounts of $CO_2$ and HCl gas. The mixture was gently refluxed under argon for 8 hours and concentrated under vacuum to yield a white solid. Crude bis(acid chloride) was added to a 250 ml three-necked flask and dissolved in anhydrous methylene chloride (90 ml). The mixture was ice-cooled and MeNHOMe.HCl (6.04 g, 0.0619 mol) was added. Dry pyridine (10 ml, 0.1292 mol) was added portionwise over a ten minute period and stirring was continued under argon for 50 minutes. Water (100 ml) was added and the layers separated. The aqueous layer was extracted with methylene chloride (75 ml) and combined organic layers were washed with water (75 ml). The organic extract was evaporated to dryness to yield an off-white solid. Recrystallization from hexanes yielded 7.44 g (65%) of pure product. $^1$H NMR ($CDCl_3$): δ 0.88 (t, J = 6.6 Hz, 3 H); 1.26 (bs, 25 H); 1.79 (m, 2 H); 3.36 (s, 6 H); 3.57 (s, 6 H); 4.00 (t, J = 6.5 Hz, 2 H); 7.30 (s, 2 H); 7.55 (s, 1 H); $^{13}$C NMR ($CDCl_3$): δ 14.08; 22.65; 25.95; 29.10; 29.34; 29.57; 29.66; 31.88; 61.14; 68.44; 116.58; 119.89; 134.99; 158.56; 168.88; IR (KBr, $cm^{-1}$): 2921; 2851; 1638; 1581; 1472; 1432; 1384; 1320; 1281; 1163; 1055; 1041.

**Diketone A.6.** Dicarboxamide **A.5** (7.068 g, 13.57 mmol) was dissolved in anhydrous THF (110 ml) and the solution cooled to 0°C. A solution of methyl lithium in diethyl ether (1.4 M, 36 ml, 50.4 mmol) was slowly added over a 10 minute period. The mixture thickened but slowly formed a clear solution.

Stirring was continued for 90 minutes. The mixture was then added to an ice-cooled solution of glacial acetic acid (3.2 ml) in water (100 ml). The layers were separated and the aqueous layer washed with diethyl ether (75 ml). Combined organic layers were concentrated under vacuum and the residue purified by flash column chromatography (15% EtOAc/petroleum ether). Yield = 5.081 g (87%); mp 68-68.5°C; $^1$H NMR ($CDCl_3$): δ 0.87 (t, J = 6.6 Hz, 3 H); 1.25 (bs, 25 H); 1.81 (m, 2 H); 2.64 (s, 6 H); 4.05 (t, J = 6.5 Hz, 2 H); 7.66 (d, J = 1.2 Hz, 2 H); 7.55 (t, J = 1.2 Hz, 1 H); $^{13}$C NMR ($CDCl_3$): δ 14.06; 22.64; 25.93; 26.72; 29.07; 29.31; 29.52; 29.55; 29.65; 31.88; 68.63; 118.29; 120.37; 138.56; 159.58; 197.12; IR (KBr, $cm^{-1}$): 3077; 2919; 2845; 1690; 1590; 1441; 1363; 1337; 1300; 1222; 1045; 969; 907; 877; Calcd for $C_{28}H_{46}O_3$: C: 78.09; H: 10.77; O: 11.14; Found : C: 78.25; H: 10.50; O: 10.74.

**Bis(bromomethyl ketone) A.7.** Diketone **A.6** (4.338 g, 0.0101 mol) was dissolved in reagent grade chloroform (100 ml) and the colorless solution cooled to 0°C. A solution of $Br_2$ in carbon tetrachloride (1.0 M, 21.7 ml, 21.7 mmol) was slowly added over 50 minutes via an addition funnel. The dark red solution was allowed to warm to room temperature whereupon it turned pale yellow in color. Stirring was continued for four hours and the solvent removed by rotary evaporation. A mixture of monobrominated, tribrominated and the desired product were separated by flash chromatography ($CHCl_3$ as eluant). Yield = 3.996 g (63%); mp 78-79°C; $^1$H NMR ($CDCl_3$): δ 0.88 (t, J = 6.5 Hz, 3 H); 1.26 (bs, 30 H); 1.83 (m, 2 H); 4.07 (t, J = 6.5 Hz, 2 H); 4.46 (s, 4 H); 7.72 (s, 2 H); 8.12 (s, 1 H); $^{13}$C NMR ($CDCl_3$): δ 14.12; 22.70; 25.96; 29.04; 29.36; 29.56; 29.60; 29.70; 30.78; 31.93; 68.92; 119.68; 121.26; 135.64; 159.97; 190.32; IR (KBr, $cm^{-1}$): 3077; 3039; 2919; 2849; 1684; 1588; 1457; 1348; 1313; 1245; 1117; 1052; 1022; 922; 880; 722; Exact Mass (FAB): Calcd. 587.1735. Found: 587.1729 (-1.2 ppm).

**A.8.** Bis(bromomethylketone) **A.7** (2.088 g, 3.548 mmol) and absolute ethanol (50 ml) were warmed in a 100 ml round-bottomed flask to yield a clear solution. *N,N'* Dimethyldithiocarbamic acid sodium salt (1.016 g, 7.095 mmol) was added in one portion immediately yielding a white precipitate. Acetone (25 ml) was added and the mixture refluxed for one hour. Starting material was still present by thin-layer chromatography so a further 0.23 g (1.61 mmol) of thiocarbamate salt was added and reflux continued for a further thirty minutes. The reaction mixture was cooled to room temperature and allowed to stand at -10°C overnight. The resulting yellow precipitate was isolated by filtration, washed well with water and dried under vacuum. The residue was dissolved in methylene chloride and passed through a short column of silica gel to yield 1.704 g (72%) of pure product as a white solid. mp 128-130°C; $^1$H NMR ($CDCl_3$): δ 0.87 (t, J = 6.4 Hz, 3 H); 1.24 (s, 28 H); 1.43 (s, 2 H); 1.80 (m, 2 H); 3.45 (s, 6 H); 3.54 (s, 6 H); 4.05 (t, J = 6.4 Hz, 2 H); 4.87 (s, 4 H); 7.77 (s, 2 H); 8.32 (s, 1 H); $^{13}$C NMR ($CDCl_3$): δ 14.07; 22.65; 25.96; 29.08; 29.33; 29.55; 29.58; 29.66; 31.89; 41.70; 45.06; 45.98; 68.77; 118.96; 120.77; 137.72; 159.74; 192.67; 196.26; Exact Mass (FAB): Calculated: 669.320953. Found: 669.3252 (+6.4 ppm).

**A.9.** Bis(*N,N'*-dialkylaminocarbodithionate) **A.8.** (2.432 g, 3.635 mmol and perchloric acid (60-62%, 30 ml) were heated together in an Erlenmeyer flask at 95-100°C. A voluminous yellow precipitate gradually formed and heating was continued with intermittent stirring for a further 15 minutes. The reaction mixture was then cooled to room temperature. Ethyl acetate (100 ml) was then added and the precipitate filtered and washed well with methanol (250 ml). The powdery yellow solid was dried overnight under vacuum to yield 2.843 g (95%) of pure bis(immonium dithiole) salt. $^1$H NMR (dmso-$d_6$): δ 0.83 (t, J = 6.3 Hz, 3 H); 1.21 (s, 30 H); 1.77 (m, 2 H); 3.55 (s, 6 H); 3.57 (s, 6 H);

4.11 (m, 2 H); 7.35 (s, 2 H); 7.50 (s, 1 H); 8.19 (s, 2 H); $^{13}C$ NMR (dmso-$d_6$): δ 13.88; 22.05; 25.43; 28.52; 28.67; 28.75; 29.00; 31.25; 46.85; 47.79; 68.40; 114.23; 116.86; 121.07; 132.10; 137.01; 159.85; 186.18.

**A.10** Bis(immonium dithiole) salt **A.9** (2.654 g, 3.245 mmol) was suspended in absolute ethanol (125 ml) and the mixture ice-cooled. Sodium borohydride (1.010 g, 0.02670 mol) was added portionwise with vigorous stirring. The ice-bath was removed and the heterogeneous mixture stirred at room temperature under argon for two hours, yielding a pale yellow solution. Solvent was removed under reduced pressure, the residue redissolved in chloroform and washed with a saturated NaCl solution. The organic layer was dried over $MgSO_4$ and concentrated to yield desired product as a yellow-brown oil (95% pure by $^1H$ NMR). Yield = 1.928 g (93%). $^1H$ NMR ($CDCl_3$): δ 0.88 (t, J = 6.5 Hz, 3 H); 1.25 (br s, 30 H); 1.77 (m, 2 H); 2.29 (s, 12 H); 3.96 (t, J = 6.4 Hz, 2 H); 6.28 (s, 2 H); 6.48 (s, 2 H); 6.90 (d, J = 1.1 Hz, 2 H); 7.17 (s, 1 H); $^{13}C$ NMR ($CDCl_3$): δ 14.11; 22.68; 26.02; 29.24; 29.35; 29.68; 31.91; 38.29; 68.21; 81.68; 112.15; 112.27; 117.31; 132.82; 135.15; 159.38.

Attempts at further purification using column chromatography (15% Ethyl acetate/ petroleum ether) on silica gel led to considerable product decomposition and gave no substantial improvement in purity.

**A.11 ($ClO_4^-$).** **A.10** (93 mg, 0.146 mmol) was suspended in absolute ethanol (5 ml) and the mixture cooled to 0°C. Concentrated sulfuric acid was slowly added dropwise over fifteen minutes. The mixture was stirred for an additional ten minutes before ethyl acetate (10 ml) was added. The filtrate was collected on a Buchner funnel and washed well with ethanol and diethyl ether yielding 70 mg of product as a fine powder that is insoluble in common organic solvents but soluble in trifluoroacetic acid. $^1H$ NMR ($CF_3COOD$ with dmso-$d_6$): δ 0.46 (bs, 3 H); 0.88 (br s, 30 H); 1.47 (br s, 2 H); 3.78 (t, J = 5.9 Hz, 2 H);

7.19 (s, 2 H); 7.44 (s, 1 H); 9.06 (s, 2 H); 11.00 (s, 2 H).

**A.11 ($HSO_4^-$).** **A.10** (362 mg, 5.68 mmol) was dissolved in diethyl ether (3 ml) and added dropwise to an ice-cooled mixture of acetic anhydride (10 ml) and 48% fluoboric acid (15 ml). The mixture was stirred for twenty minutes and the resulting fine red solid filtered and washed well with diethyl ether. $^1H$ NMR and UV suggests a dimeric tetrathiafulvalene structure.

**References**


(1) Bryce, M. R. *Chem. Mater.* **1995**, *5*, 1481.

(2) Williams, J. M.; Schultz, A. J.; Geiser, K.; Carlson, D.; Aravinda, M.; Kini, M.; Hau Wang, H.; Kwok, W.-K.; Whangbo, M.; Schirber, J. E. *Science* **1991**, *252*, 1501.

(3) Wudl, F. *Acc. Chem. Res.* **1984**, *17*, 227-232.

(4) Rovira, C.; Veciana, J.; Santaló, N.; Tarrés, J.; Cirujeda, J.; Molins, E.; Llorca, J.; Espinosa, E. *J. Org. Chem.* **1994**, *59*, 3307.

(5) Benz, M. E.; Tabakovic, I.; Miller, L. L. *Chem. Mater.* **1994**, *6*, 351.

(6) West, A. P., California Institute of Technology, unpublished results.

(7) Takamizawa, A.; Hirai, K. *Chem. Pharm. Bull.* **1969**, *17*, 1924.

(8) Kaplan, M. L.; Haddon, R. C.; Wudl, F. *J. Chem. Soc. Chem. Commun.* **1977**, 388.

(9) Trinh, V. Q.; Van Hinh, L.; Schukat, G.; Fanghänel, E. *J. Prakt. Chemie.* **1989**, 826.

(10) Iyoda, M.; Kuwatani, Y.; Ueno, N.; Oda, M. *J. Chem. Soc. Chem. Commun.* **1992**, 158.

(11) Mizouchi, H.; Ikawa, A.; Fukutome, H. *J. Amer. Chem. Soc.* **1995**, *117*, 3260.

(12) Sugimoto, T.; Yamaga, S.; Nakai, M.; Nakatsuji, H.; Yamauchi, J.; Fujita,

H.; Fukutome, H.; Ikawa, A.; Mizouchi, H.; Kai, Y.; Kanehisa, N. *Adv. Mater.* **1993**, *5*, 741.

# Appendix B

## Synthetic Progress Towards a Potential High-Spin Organometallic Polymer: Poly(*meta*-Nickel Dithiolene).

Transition metals have served as spin sources for magnetic materials since the discovery of lodestone. They enjoy several advantages over organic-based materials, most notably spin stability and high polarizability. Traditional magnets, however, are insoluble and infusible and this imposes a considerable restraint on their potential use in the new information age. The study of "molecular magnets" continues to be an active area of research.[1-5] Such rationally designed high-spin substances are often soluble and may be well characterized. In addition, due to their paramagnetic nature, molecular magnets do not need a separate spin-introduction step. Bulk ferromagnetism has been demonstrated in some instances.[6]

Elaboration of high-spin metallic clusters into a bulk ferromagnet, however, is not an easy proposition. Magnetic properties of these systems are often dominated by crystal packing phenomena and can be sensitive to nominal perturbations such as changing counterions. A hybrid approach employing transition-metal spin sources high-spin coupled through a polyradical organic framework is attracting increasing attention in the literature.[7]

There has been little attention devoted to the synthesis of high-spin polymeric organometallic materials. High conductivity has been demonstrated in several organometallic macromolecules, yet there has been little effort devoted to the ferromagnetic alignment of metallic spins in a polymeric framework.

*Para*-linked transition metal bis(dithiolene) complex polymers, (Figure B-1) have been described and exhibit several attractive features most notably solubility in both aqueous and organic solvents and electrochemical reversibility.[8,9] In addition, molecular orbital calculations suggest that the HOMO of the singly reduced species is ligand-based and has over 50% C 2p

character, implying that ferromagnetic coupling amongst spins may be quite strong.

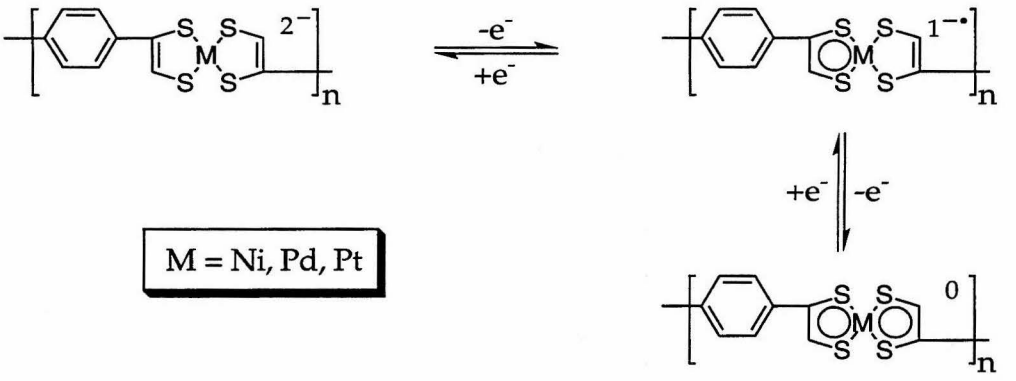
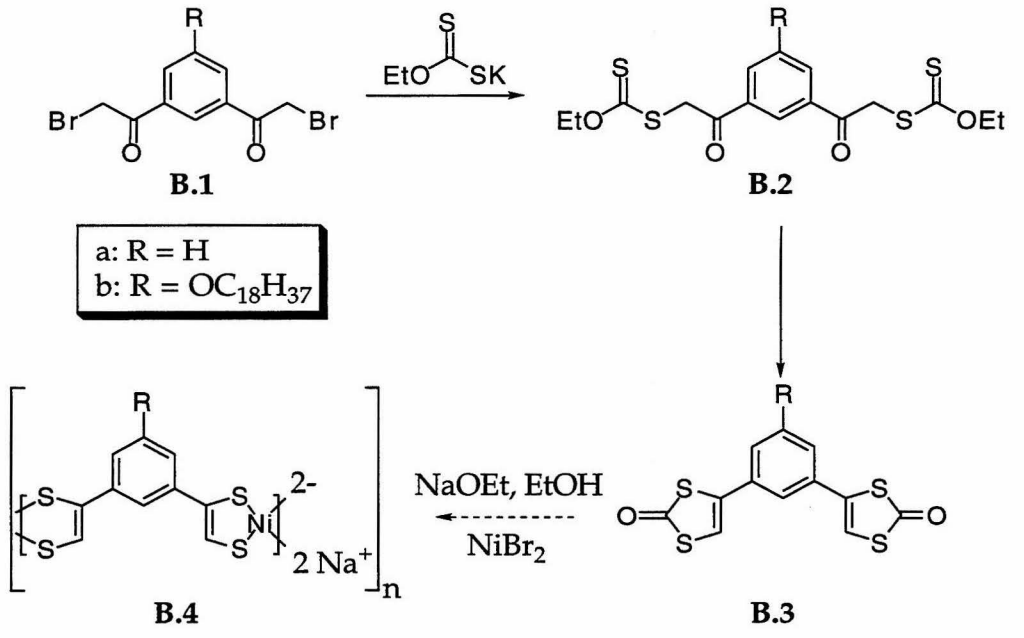



**Figure B.1.** Redox cycling between different redox states of transition metal dithiolenes.

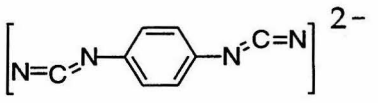
Ligands suitable for the incorporation of transition metals into a high-spin organic topology have been synthesized, starting from bis(acetyl bromides) **B.1** as outlined in Scheme B-1. The synthesis of **B.1b** has already been described in Chapter 2 of this dissertation.[10] Final complexation with the metal has not been attempted.

**Scheme B-1**




**Outlook**

Magnetic behavior of the all *para* version of **B.4** has not been reported. Closely related poly(benzodithiolenes), however, have a weak singlet preference.[11] There have been recent reports of a remarkably strong antiferromagnetic interaction ($J \geq -400$ cm$^{-1}$) in dinuclear ruthenium pentaammine complexes incorporating a 1,4-dicyanamidobenzene dianion (dicyd$^{2-}$) bridging ligand.[12] Superexchange metal-metal coupling is strong enough in some derivatives to render the complex diamagnetic *at room temperature*. The corresponding 1,3 isomer may show significant ferromagnetic coupling and cast new light on how to achieve high-spin coupling of metals attached to organic ligands. Synthesis of the appropriate 1,3 ligand is trivial, the bimetallic complex may show novel ferromagnetic behavior.



**DICYD $^{2-}$**

**Experimental**

1,3-Bis(bromoacetyl) benzene **B.1a**. 1,3-Diacetylbenzene (4.978 g, 30.69 mmol) was placed in a 250 ml round-bottomed flask. Reagent grade chloroform (30 ml) was added and the resulting solution cooled to -10°C. $Br_2$ (1.0 M in $CCl_4$, 65 ml, 65 mmol) was added dropwise over a 40 minute period. The reaction mixture was allowed to slowly rise to room temperature. The color had changed from deep red to pale yellow after one hour. Stirring was continued overnight. The mixture was then evaporated and the residue chromatographed on silica gel using methylene chloride as an eluant to yield 5.87 g (60%) of pure product. $^1$H NMR ($CDCl_3$): δ 4.52 (s, 4 H); 7.67 (t, J = 7.8 Hz, 1 H); 8.23 (d, J = 7.8 Hz, 2 H); 8.57 (s, 1 H); $^{13}$C NMR ($CDCl_3$): δ 30.41; 129.12; 129.52; 133.64; 134.60; 190.31; GC/MS: 320 ($M^+$, 1); 227 (98); 225 (100); 146 (10); 118 (31); 104 (17).

**B.2a.** To a mixture of **B.1a** (5.466 g, 17.1 mmol) and acetone (60 ml) was added *O*-ethylxanthic acid (5.500 g, 34.31 mmol) and the mixture brought to reflux for 48 hours. The mixture was then added to water (100 ml). Chloroform (80 ml) was added and the organic layer separated. The aqueous layer was extracted with 100 ml of chloroform, the organic extracts combined and washed with water (100 ml). The solvent was evaporated to yield 6.10 g (89%) of pure product; mp 87-88°C; $^1$H NMR ($CDCl_3$): δ 1.40 (t, J = 7.1 Hz, 6 H); 4.64 (q, J = 7.1 Hz, 4 H); 4.69 (s, 4 H); 7.67 (t, J = 7.8 Hz, 1 H); 8.26 (d, J = 7.8 Hz, 2 H); 8.65 (s, 1 H); $^{13}$C NMR ($CDCl_3$): δ 13.62; 43.21; 70.79; 128.13; 129.41; 132.98; 136.40;

191.57; 212.79.

**B.3a.** Bisxanthate **B.2a** (5.90 g, 14.66 mmol), glacial acetic acid (70 ml) and 30% HBr in glacial acetic acid (45 ml) were combined in a 250 ml flask. The solid dissolved upon refluxing and a precipitate gradually formed. Reflux was continued for 3 hours and the mixture cooled and filtered. Methylene chloride (150 ml) was added to the filtrate, the organic solution washed with water (100 ml) and the organic layer concentrated to yield 1.81 g (40%) of sparingly soluble product.

**B.2b.** Bis(acetyl bromide) **B.1b** (3.620 g, 6.152 mmol) and acetone (60 ml) were added to a 100 ml three-necked flask. *O*-ethyl xanthic acid potassium salt (1.991 g, 12.420 mmol) was added and the mixture refluxed for 12 hours. The yellow heterogeneous mixture was cooled and partitioned between chloroform (100 ml) and water (60 ml). The aqueous layer was extracted further with chloroform (60 ml) and combined organic layers were concentrated. The resulting brown residue was subjected to flash chromatography (chloroform as eluant) to yield 3.182 g (77%) of bisxanthate as a pale yellow solid. mp 64-65°C; $^{1}$H NMR ($CDCl_3$): δ 0.86 (t, J = 6.8 Hz, 3 H); 1.24 (bs, 30 H); 1.80 (m, 2 H); 4.07 (t, J = 6.5 Hz, 2 H); 4.63 (q, J = 7.1 Hz, 4 H); 4.65 (s, 4 H); 7.73 (s, 2 H); 8.19 (s, 1 H); $^{13}$C NMR ($CDCl_3$): δ 13.68; 14.01; 22.61; 25.94; 29.05; 29.30; 29.51; 29.54; 29.60; 29.64; 31.86; 43.32; 68.91; 70.83; 119.05; 120.37; 137.58; 159.92; 191.56; 212.92; IR (KBr, $cm^{-1}$): 3092; 2976; 2922; 2850; 1695; 1588; 1471; 1437; 1351; 1339; 1220; 1112; 1062; 1043; 1004; 982; 899; 713; Calculated for $C_{37}H_{54}S_4O_5$: C:60.86; H: 8.11; S: 19.11. Found: C: 60.97; H: 8.11; S: 19.05; Exact Mass: Calculated 671.2932. Found: 671.2893 (-5.8 ppm).

**B.3b.** A mixture of bisxanthate **B.2b** (1.560 g, 2.325 mmol), glacial acetic acid (30 ml) and a solution of HBr in glacial acetic acid (30%, 7 ml) was brought to reflux forming a red solution. Reflux was continued for three hours, cooled

and the solvent removed under vacuum. The residue was dissolved in chloroform (150 ml) with gentle warming and the solution washed with water. The organic layer was concentrated to yield 1.214 g (90%) of gray-white solid shown by NMR to be the desired product. The material may be further purified by dissolving it in methylene chloride, passing it through a short column of silica gel and recrystallization from *iso*-propanol. mp 121-123°C; $^1$H NMR ($CDCl_3$): δ 0.86 (t, J = 6.7 Hz, 3 H); 1.23 (bs, 30 H); 1.79 (m, 2 H); 3.98 (t, J = 6.5 Hz, 2 H); 6.87 (s, 2 H); 6.91 (d, J = 1.5 Hz, 2 H); 7.01 (t, J = 1.5 Hz, 1 H); IR (KBr, $cm^{-1}$): 3095; 2952; 2915; 2845; 1664; 1635; 1594; 1472; 1431; 1306; 1182; 1542; 1072; 885; 758; Calculated for $C_{30}H_{42}S_4O_3$: C:62.24; H: 7.31; S: 22.15. Found: C: 62.36; H: 7.38; S: 22.03; Exact Mass (FAB): Calculated 579.2095. Found: 579.2116 (+3.7 ppm).

**References**


(1) Kahn, O.; Hendrickson, D. N.; Iwamura, H.; Veciana, J. In *Magnetic Molecular Materials;* D. Gatteschi, O. Kahn, J. S. Miller and F. Palacio, Ed.; Kluwer Academic Publishers: The Netherlands, 1991; pp 385-388.

(2) Kahn, O.; Kröber, J.; Jay, C. *Adv. Mater.* **1992**, *4*, 718-728.

(3) Gatteschi, D.; Sessoli, R. *J. Magn. Magn. Mater.* **1992**, *1104-107*, 2092-2095.

(4) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201-220.

(5) *Chemistry and Physics of Molecular Based Magnetic Materials. Mol. Cryst. Liq. Cryst.*; Iwamura, H.; Miller, J. S., Ed.; Gordon and Breach Publishers: USA, 1993; Vol. 232, pp 360.

(6) Miller, J. S.; Calabrese, J. C.; Rommelmann, H.; Chittipeddi, S. R.; Zhang, J. H.; Reiff, W. M.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 769-781.

(7) Iwamura, H.; Inoue, K.; Hayamizu, T. *Pure and App. Chem.* **1996**, *68*, 243.

(8) Wang, F.; Reynolds, J. R. *Macromolecules* **1988**, *21*, 2887.

(9) Wang, F.; Reynolds, J. R. *Macromolecules* **1990**, *23*, 3219.

(10) See Appendix A of this thesis.

(11) Dirk, C. W.; Bousseau, M.; Barrett, P. H.; Moraes, F.; Wudl, F.; Heeger, A. J. *Macromolecules* **1986**, *19*, 266.

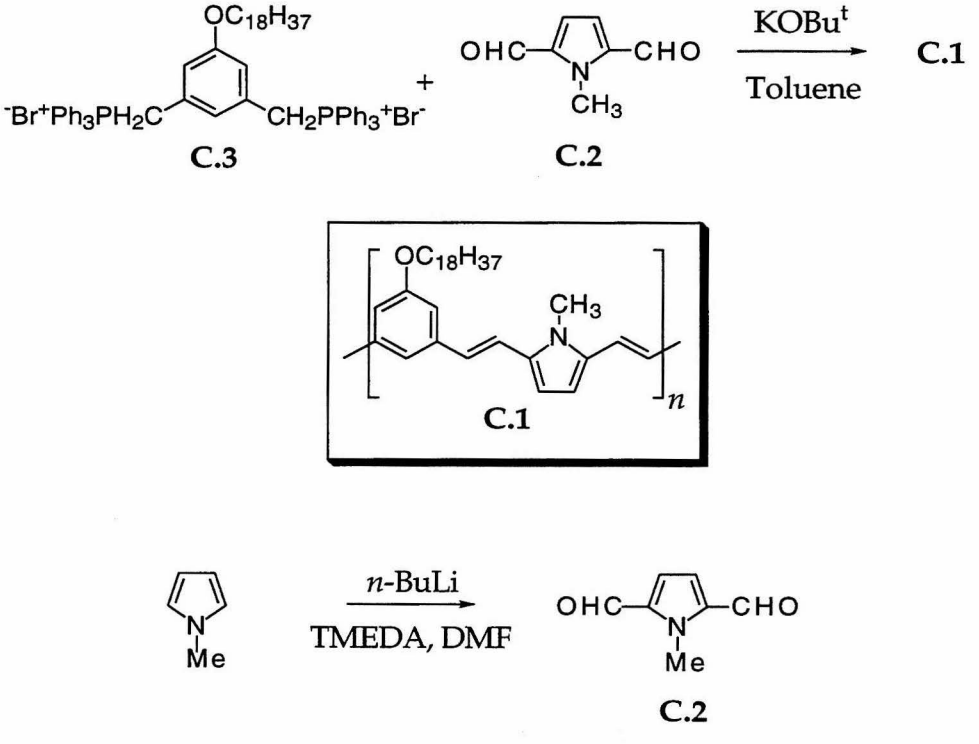
(12) Aquino, M. A. S.; Lee, F. L.; Gabe, E. J.; Bensimon, C.; Greedan, J. E.; Crutchley, R. J. *J. Amer. Chem. Soc.* **1992**, *114*, 5130.

# Appendix C

## An Investigation of Solubility and Magnetic Properties of Pyrrole-Based Prototypes for the Polaronic Ferromagnet.

A number of linear and cross-linked pyrrole-based systems were studied. *N*-Methyl pyrrole has a substantially lower oxidation potential than thiophene,[1] and it was hoped that this would increase spin concentration upon $I_2$ doping. Poly-*meta*-phenylene vinylene *N*-methyl pyrrole vinylene **PMPVMPV, C.1**, was synthesized by Wittig chemistry (Scheme C-1) from dialdehyde **C.2** and subjected to a solution-phase $I_2$ doping protocol. Doped polymer did not contain a significant number of spins, suggesting that polaron stability need not necessarily scale with redox potential. Oxidation with $AgClO_4$ gave 1% spins and $S = 0.9$.

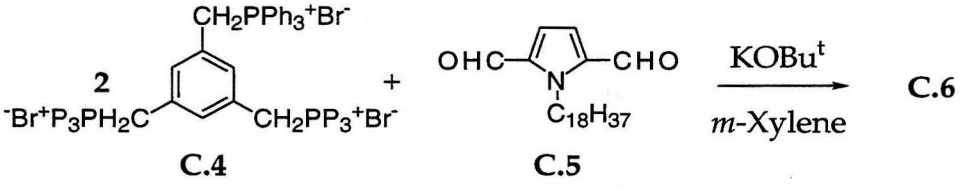
**Scheme C-1**




Cross-linking strategies employing *N*-octadecylpyrrole dialdehyde **C.5** were

also pursued. When 2 equivalents of trisphosphonium salt **C.4** were treated with 3 equivalents of **C.5** in refluxing xylene with added potassium *tert*-butoxide, cross-linked polymer **C.6** immediately precipitated from the reaction mixture (Scheme C-2). A less ambitious strategy employing 6 equivalents of **C.5** with 2 equivalents of **C.4** and 3 equivalents of bisphosphonium salt **C.3** furnished a material that is sparingly soluble in organic solvents (Scheme C-1). GPC analysis employing UV detection suggests that the molecular weight is of the order of $10^5$; this is consistent with a cross-linked polymeric structure. SQUID results were unexceptional: this material when doped with iodine gives measurable spin concentration of approximately 0.4% and $S \approx 1.5$.

**Scheme C-2**





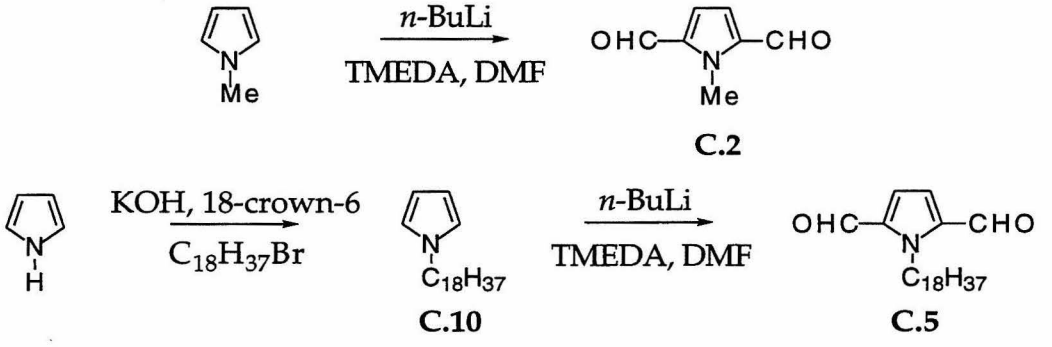
**Discussion**

These studies demonstrate that only moderate amounts of cross-linking will be tolerated by these systems. SQUID results hint that a cross-linked system may stabilize spins, but data cited above are the result of a single experiment in each case. It is anticipated that significant improvements in *S* value will only be seen in cross-linked systems that employ more stable spin

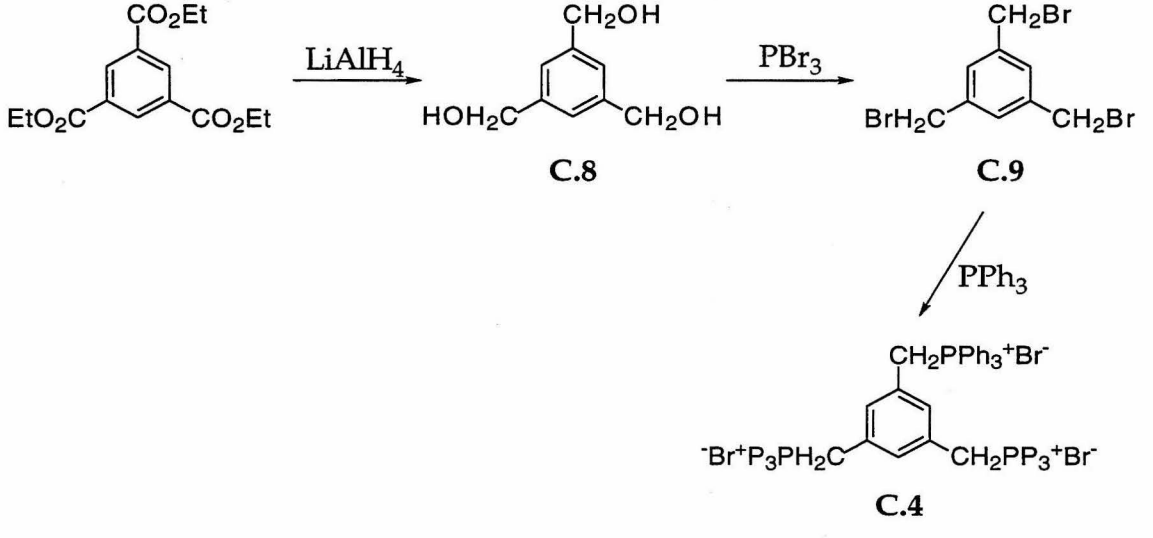
sources.

Synthesis of the appropriate aldehydes is described in Scheme C-3. Synthesis of trisphosphonium salt is described in Scheme C-4. Synthesis of **C.3** has been described.[2]

**Scheme C-3**




**Scheme C-4**



**Synthesis**

**Poly-*meta*-phenylene-*N*-methyl pyrrole vinylene, (C.1).** Bisphosphonium salt **C.3** (1.6860 g, 1.5951 mmol) and dialdehyde **C.2**, (215.6 mg, 1.5956 mmol) were combined in a 50 ml Schlenk flask. Freshly distilled toluene (20 ml) was added. To the heterogeneous mixture was added a solution of potassium *tert*-butoxide (1.0 M, 4.5 ml, 4.5 mmol) in THF. The resulting deep red solution was stirred for fifteen minutes at room temperature and then brought to reflux under argon for a total of three days. The yellow-brown reaction mixture was then cooled to room temperature, the solvent evaporated and the residue soxhlet extracted with methanol for seventy-two hours to yield 615 mg (81%) of yellow polymer; $^1$H NMR ($CD_2Cl_2$): d 0.87 (br s, 3 H); 1.25 (br s, 30 H); 1.78 (br s, 2 H); 3.4 - 4.1 (br m, 5 H); 6.0 - 7.2 (br m, 9 H); IR (KBr, $cm^{-1}$): 3021; 2922; 2850; 1618; 1579; 1459; 1302; 1259; 1055; 943; 752; 654; GPC ($CH_2Cl_2$): $M_n$ = 4380; $M_w$ = 7840; PDI = 1.79 (Monomer MW = 476 g/ mol); UV($CH_2Cl_2$): $\lambda_{max}$ = 415 nm; Calculated for $C_{33}H_{49}NO$: C: 83.31; H: 10.38; N: 2.94; O:3.36; Found: C: 81.24; H: 10.29; N: 2.53. Further extraction with acetone (12 hours) yielded a small amount of soluble oligomers ($M_n$ = 1710; $M_w$ = 2820) and an insoluble fraction which was further extracted with hexanes, redissolved in methylene chloride and passed through a short column of silica gel to yield 265 mg of high molecular weight polymer. GPC ($CH_2Cl_2$, UV): $M_n$ = 5680; $M_w$ = 10820; PDI = 1.90.

***N*-Methyl pyrrole-2,5 dialdehyde (C.2).** In a 250 ml three-necked flask fitted with a magnetic stirbar were combined freshly distilled *N*-methyl pyrrole (1.736 g, 0.0214 mol), anhydrous hexane (75 ml), and TMEDA (9.2 g, 0.08 mol). The pale yellow solution was cooled to 0°C and *n*-butyl lithium in hexanes (2.5 M, 32 ml, 0.08 mol) was slowly added. The cooling bath was then removed, the mixture brought to reflux under argon for 75 minutes, and then

cooled to room temperature. Dry THF (20 ml) was added and the yellow suspension was cooled to -78°C. Anhydrous DMF (9.4 g, 0.13 mol) was added in one portion, the mixture stirred for one hour, allowed to warm to room temperature and stirred for a further hour. It was then added to an ice-cold 2 M HCl solution (200 ml), and diethyl ether (100 ml) was added. The layers were separated and the aqueous layer extracted with fresh diethyl ether. Combined organic extracts were then dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography using 15% ethyl acetate/ petroleum ether as eluant to yield 755 mg (32%) of bisaldehyde. mp 95-97°C; $^1$H NMR ($CDCl_3$): δ 4.28 (s, 3 H); 6.95 (s, 2 H); 9.85 (s, 2 H); GC/MS: 137 ($M^+$, 100); 136 (M-1, 28); 108 (17); 68 (31); 53 (47); $^{13}$C NMR ($CDCl_3$): δ 34.43; 121.66; 136.28; 182.27.

**Benzene-1,3,5-trimethanol (C.8).**[3] Benzene-1,3,5-trimethyl ester (1.12 g, 4.44 mmol) was dissolved in anhydrous THF (50 ml) and the resulting solution added dropwise via an addition funnel to a mixture of lithium aluminum hydride (1.12 g, 4.44 mmol) and THF (50 ml) in a 250 ml three-necked flask. The solution was warmed gently, initially went tan in color and then pale gray. The mixture was refluxed under argon for 24 hours and then cooled. Water (1 ml), 10% NaOH (1 ml) and water (20 ml) were then added successively, the mixture ws stirred overnight and then filtered. The solvent was then removed in vacuum to yield 724 mg (97%) of tris alcohol as an oily solid. $^1$H NMR ($D_2O$): δ 7.26 (s, 3 H); 4.59 (s, 6 H); $^{13}$C NMR ($D_2O/CD_3OD$): δ 63.93; 125.77; 141.35; GC/MS: $M^+$ 168 (100); 150 (22); 151 (8); 149 (9); 137(7).

**1,3,5-tribromomethylbenzene (C.9).**[3] 1,3,5 benzenetrimethanol **C.8** (913 mg, 5.43 mmol) was suspended in anhydrous diethyl ether (55 ml) and the reaction mixture cooled to 0°C in an ice-bath. Phosphorous tribromide (23.40 g, mmol) dissolved in diethyl ether (50 ml) was slowly added dropwise over

45 minutes with ice-cooling. The mixture was stirred overnight and cautiously added to 200 ml of ice-water with vigorous stirring. The organic layer was separated and the aqueous layer extracted with diethyl ether (3 x 80 ml). The combined ether extracts were washed with an aqueous solution of sodium carbonate. Purification was effected by column chromatography (5% EtOAc/petroleum ether). The tribromide was recrystallized from hexanes to furnish 940 mg (48.4%) of desired product. $^1$NMR ($CDCl_3$): δ 4.45 (s, 6 H); 7.35 (s, 3 H); $^{13}$C NMR ($CDCl_3$): δ 32.17; 129.54; 139.01.

**1,3,5-Benzene-(triphenylphosphonium bromide) (C.4).** 1,3,5-Tribromomethylbenzene **C.9** (569 mg, 1.59 mmol), triphenylphosphine (1.305 g, 4.98 mmol) and anhydrous acetonitrile (150 ml) were combined in a three-necked 250 ml flask and the solution was brought to reflux under argon. A white precipitate slowly formed and reflux continued for a total of 24 hours. The white solid was collected by filtration and recrystallized from methanol-diethyl ether (twice), placed in a drying pistol and dried over refluxing xylenes at 0.01 torr for 24 hours to yield 961 mg (53.8%) of pure product. $^1$H NMR ($CD_3OD$): δ 7.87 (m, 9 H); 7.65 (m, 18 H); 7.52 (m, 18 H); 6.77(s, 3 H); 4.74 (d, J = 15.3 Hz, 6 H); $^{13}$C NMR ($CD_3OD$): δ 29.72 (d, J = 49.07 Hz); 118.55 (d, J = 86.06 Hz); 131.63 (d, J = 13.59 Hz); 134.56 (d, J = 3.77 Hz); 135.07; 135.20; 136.54.

***N*-Octadecylpyrrole (C.10).**[4] Pyrrole (4.00 g, 0.0596 mol), 18-crown-6 (530 mg, 3 mol%) and potassium hydroxide (4.1 g, 0.07 mol) were combined in a 250 ml three-necked flask. Benzene (50 ml) was added and the mixture heated to reflux for two hours. Octadecyl bromide (20.0 g, 0.060 mmol) was dissolved in 70 ml of reagent grade benzene and added to the dark-brown reaction mixture at room temperature. The initiation of the reaction was indicated by the formation of a potassium bromide precipitate. $^1$H NMR and TLC showed some bromide remaining and thus, a mixture of pyrrole ( 2 g),

potassium hydroxide (2.2 g) and reagent grade benzene (25 ml) was added to the reaction mixture. Reflux was then continued for 20 hours, the heterogeneous mixture was gravity-filtered and concentrated under vacuum to yield a brown solid. Flash chromatography (3% EtOAc/petroleum ether) yielded 15.72 g (82%) of pure product as a white solid. mp 35-36°C; $^1$H NMR ($CDCl_3$): δ 0.88 (t, J = 6.6 Hz, 3 H); 1.25 (bs, 30 H); 1.73 (m, 2 H); 3.85 (t, J = 7.2 Hz, 2 H); 6.12 (t, J = 2.1 Hz, 2 H); 6.63 (t, J = 2.1 Hz, 2 H); $^{13}$C NMR ($CDCl_3$): δ 14.13; 22.71; 26.79; 29.23; 29.29; 29.52; 29.59; 29.65; 29.72; 31.60; 31.95; 49.63; 107.74; 120.41.

**N-Octadecyl pyrrole-2,5 dialdehyde (C.5).** *N*-Octadecyl pyrrole **C.10** (1.604 g, 5.019 mmol) was dissolved in anhydrous hexanes (13 ml) in a 50 ml three-necked flask. TMEDA (3.9 g, 0.033 mol) was added and the mixture cooled to 0°C. *n*-Butyl lithium in hexanes (2.5 M, 13.5 ml, 0.034 mmol) was added dropwise over a 5 minute period, the mixture allowed to rise to room temperature and refluxed under argon for 90 minutes forming a thick yellow suspension. Upon subsequent cooling to room temperature, anhydrous THF (6 ml) was added. The reaction mixture was cooled to -40°C and DMF (5.7 g, 0.078 mmol) was added in one portion. It was stirred at this temperature for 20 minutes and allowed to rise to room temperature. The resulting clear solution was stirred at room temperature for 24 hours and added to 2N HCl (110 ml) at 0°C. The mixture was brought to pH 6 by the addition of solid sodium bicarbonate. Diethyl ether (100 ml) was added, the organic layer separated and washed with water. Further extraction of the aqueous layer with diethyl ether and concentration of the organic extracts yielded a mixture of starting material, monoaldehyde and desired bisaldehyde. Purification by flash chromatography (3% EtOAc/petroleum ether) yielded 498 mg (26.4%) of pure product. $^1$H NMR ($CDCl_3$): δ 0.88 (t, J = 6.9 Hz, 3 H); 1.25 (bs, 30 H); 1.71

(m, 2 H); 4.75 (t, 2 H); 6.95 (s, 2 H); 9.83 (s, 2 H); $^{13}C$ NMR ($CDCl_3$): δ 14.08; 22.67; 26.46; 29.21; 29.50; 29.54; 29.57; 31.63; 31.91; 46.75; 121.85; 135.95; 181.85; IR (NaCl, $cm^{-1}$): 718; 792; 814; 827; 982; 1027; 1183; 1160; 1388; 1415; 1466; 1510; 1661; 1686; 2849; 2918; GC/MS: 375 ($M^+$, 100); 376 (26); 346 (91); 150(17); 136 (26); 124 (18); Calculated for $C_{24}H_{41}NO_2$: C: 76.75; H: 11.00; N: 3.73. Found: C: 76.46; H: 10.76; N: 4.04.

**Cross-linked Polymer C.6.** Triphosphonium salt **C.4** (704.9 mg, 0.6161 mmol) and *N*-octadecyl 2,5-dialdehyde (347.0 mg, 0.9239 mmol) were combined in a clean dry 50 ml Schlenk flask fitted with a magnetic stirrer. The flask was evacuated, filled with argon and fitted with a rubber septum. Anhydrous *m*-xylene (18 ml) was added via syringe. The heterogeneous mixture was stirred at room temperature and potassium *tert*-butoxide (1.0 M in THF, 2.45 ml, 2.45 mmol) was added dropwise over a 10 minute period. The yellow mixture turned red upon formation of the phosphonium ylide. The rubber septum was replaced by a reflux condenser and the solution warmed to 100°C. It was heated at this temperature for 18 hours and then refluxed for a further 24 hours. The solvent was then removed under vacuum and the resulting solid placed in a soxhlet thimble. It was extracted with methanol for 3 days and with benzene for 12 hours to yield 235 mg (60.6 %) of yellow solid that is insoluble in all common organic solvents. Calculated: C: 85.86; H: 10.81; N: 3.34; Found: C: 84.16; H: 11.05; N: 2.68; P: 0.54; O: 0.73.

**Cross Linked Polymer C.7.** To a clean, dry 50 ml Schlenk flask fitted with a magnetic stirbar was added bisphosphonium salt **C.3** (1.1482 g, 1.0863 mmol), triphosphonium salt **C.4** (0.8294 g, 0.7252 mmol) and *N*-octadecyl 2,5-bisaldehyde **C.5** (0.8170 g, 2.1753 mmol). The flask was alternatively evacuated and filled with argon. The stopper was replaced by a rubber septum and

anhydrous toluene (30 ml) was added. The white suspension was stirred for 15 minutes and potassium *tert*-butoxide (1.0 M in THF, 6.8 ml, 6.8 mmol) was slowly added over a 3 minute period via syringe. The deep red solution was brought to reflux under argon. Reflux was continued for 72 hours, the reaction mixture cooled and added to methanol (125 ml). The voluminous precipitate was redissolved in toluene and precipitated with methanol. The suspension was centrifuged overnight and dried under vacuum to yield 382 mg (31%) of yellow polymer. $^1$H NMR ($CDCl_3$): δ 0.86 (bs, 21 H); 1.26 (bs, 270 H); 1.80 (bs, 18 H); 4.03 (bs, 18 H); 6.60 (bs, 15 H); 6.93 (bs, 24 H); 7.75 (bs, 12 H).

**References**

(1) Rohde, N.; Eh, M.; Geissler, U.; Hallensleben, M. L.; Voigt, B.; Voigt, M. *Adv. Mater.* **1995**, *7*, 401.

(2) See Chapter 2 of this dissertation.

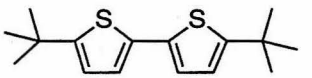
(3) Cochrane, W. P.; Pauson, P. L.; Stevens, T. S. *J. Chem. Soc.* **1968**, *C*, 630.

(4) Santaniello, E.; Farachi, C.; Ponti, F. *Synthesis* **1979**, 617.

# Appendix D

## An EPR Investigation of Thiophene Model Compounds for the Polaronic Ferromagnet.

Relatively mild methods of obtaining well-resolved EPR spectra of thiophene radical cations have recently been reported.[1,2] For example, simple photolysis of 5,5'-Bis(*tert*-butyl)-2,2'-bithiophene **D.1** in trifluroacetic acid (TFA) *at room temperature* gives a clean spectrum of the corresponding radical cation.[3]



**D.1**

The stability of radical cations in acidic media can be explained by Figure D-1.[4] The primary decomposition route of radical cations is believed to be initial loss of a proton yielding a neutral radical, M•. Subsequent hydrogen abstraction yields a highly reactive cation, which then reacts with a nucleophile D. Strongly acidic media inhibit the initial proton loss.

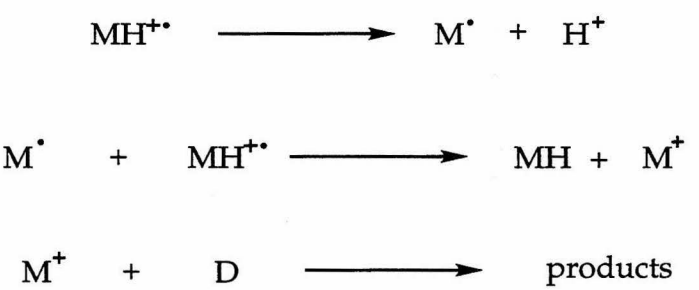
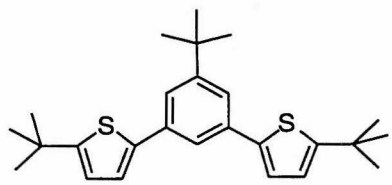



**Figure D-1.** Decomposition route of radical cations.

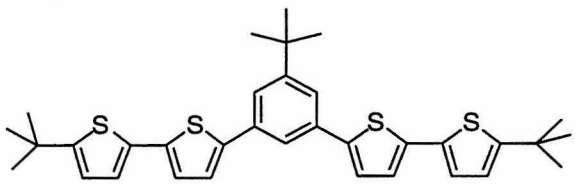
It has been of interest for some time in this group to determine the singlet-triplet gap of model compounds for the polaronic ferromagnet as an estimation of the triplet preference, *J*, of model triplets would serve as a useful way of calibrating variable temperature SQUID data of polymeric

analogs (see Chapter 2).

Model compounds **D.2** and **D.3** were prepared as outlined in Schemes D-1 and D-2. Thiophene itself undergoes polymerization at the 2 and 5 positions so these were endcapped with bulky *tert*-butyl groups.



**D.2**



**D.3**

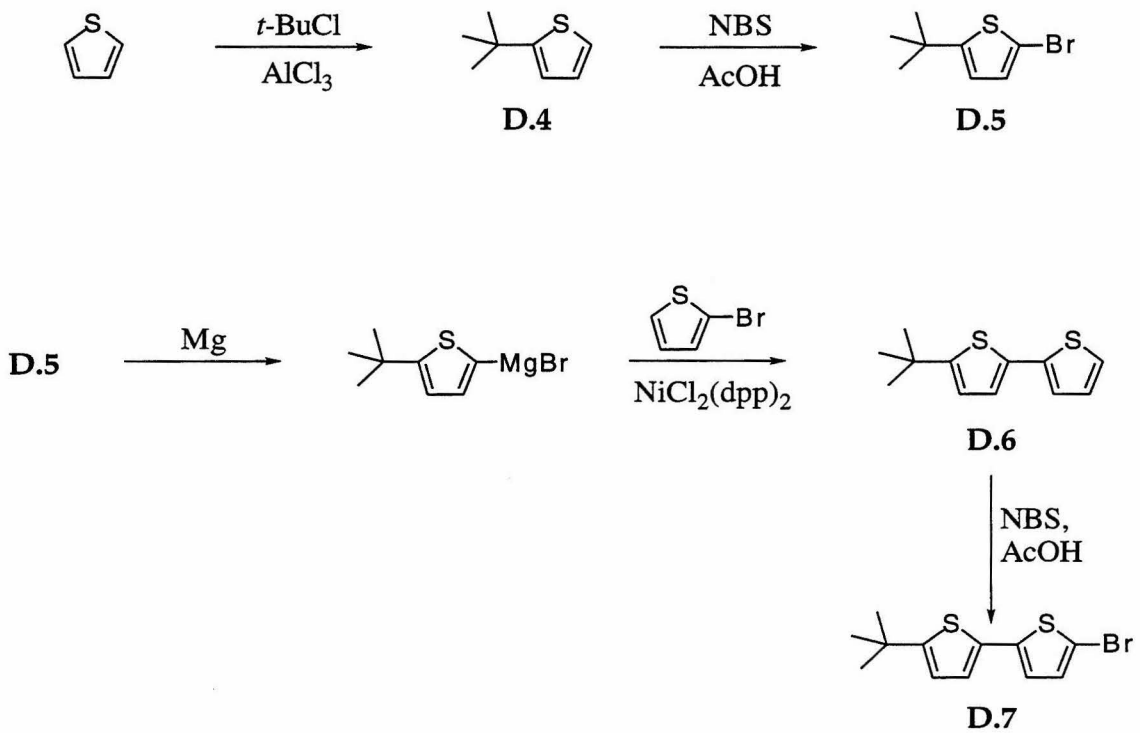
The general features of the published spectrum of **D.1** could be reproduced by dissolving in TFA and degassing the mixture (Figure D-2). Signal intensity increased by a factor of 10-20 upon photolysis for five minutes. The EPR signal gradually disappeared upon standing, but could be readily regenerated by resuming photolysis. Not surprisingly, all attempts to obtain a resolved spectrum of the frozen solution at 77 K, or to photolyze a frozen solution failed.

As neither **D.2** nor **D.3** are soluble in TFA alone, a number of solvent mixtures were investigated. When **D.1** was dissolved in 1:1 methylene chloride/TFA and photolyzed at room temperature, a broad spectrum lacking hyperfine detail was obtained. Increase in signal intensity upon photolysis mirrored that of **D.1** in TFA alone. Several other solvents were mixed with TFA but no improvement in resolution was obtained upon photolysis. It became clear at this stage that photolysis in fluid media was not going to be a suitable means of generating well-resolved EPR spectra of **D.2** and **D.3**.

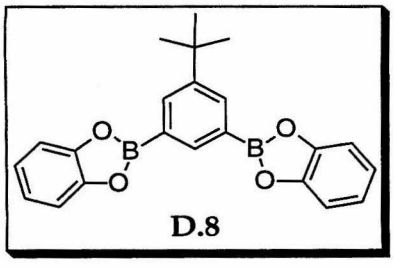
Two different chemical oxidation protocols were followed: namely $AlCl_3$ and $SbCl_5$. The former proved to be somewhat ineffective in generating strong

well-resolved spectra of **D.1**. A single chemical oxidation of **D.3** was attempted using $SbCl_5$ in methylene chloride. A strong spectrum approximately 100 G wide was obtained (Figure D-3) but there was no evidence for a half-field transition, even at 4.5 K. Furthermore, it proved impossible to add either oxidant in stoichiometric amounts because of the very low concentrations employed. Further studies on **D.2** and **D.3** were not pursued.

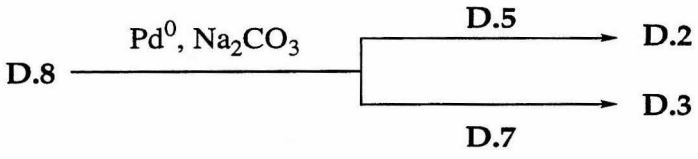
**Scheme D-1**



**Scheme D-2**



**D.8**



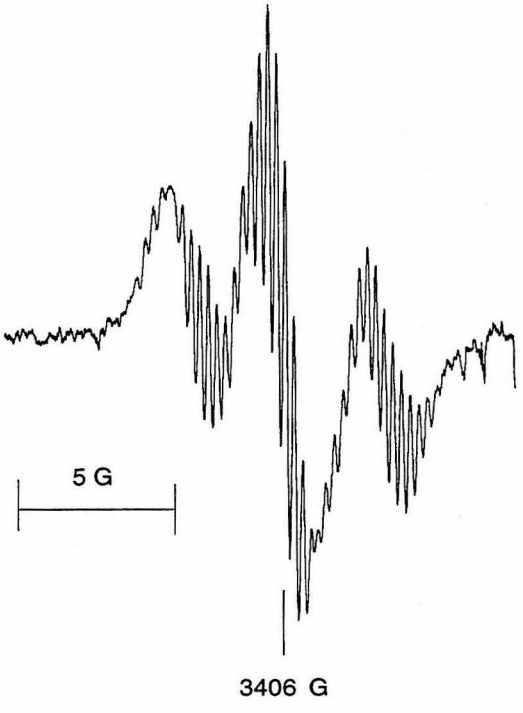




**Figure D.2.** Room temperature EPR spectrum of **D.1** photolyzed in TFA.

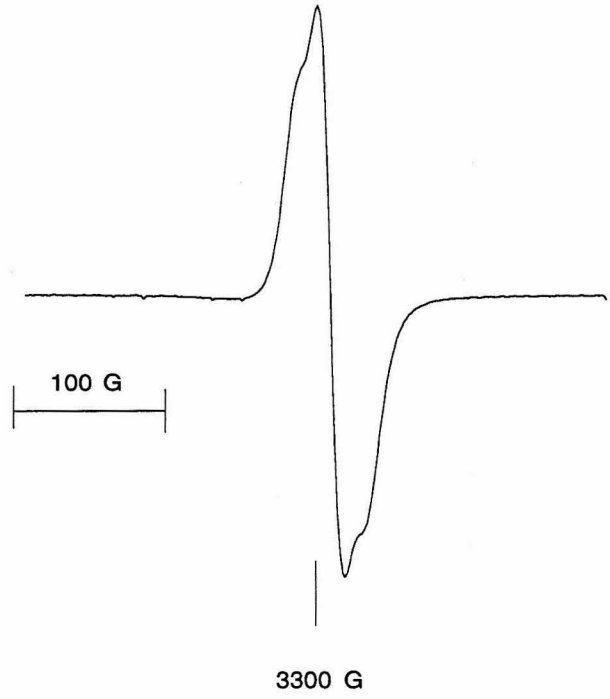



**Figure D-3.** 4.5 K EPR spectrum of **D.3** oxidized with $SbCl_5$ in $CH_2Cl_2$.

**Experimental**

EPR samples were degassed with several freeze-pump-thaw cycles. EPR spectra were acquired on a Varian E-line Century series EPR spectrometer at 100kHz modulation frequency, X-band microwave frequency 9.18-9.29 GHz. $\Delta m_s$ = 1 spectra were observed centered at g = 2.00. An Oxford Instruments ESR-900 liquid helium cryostat was used for variable-temperature experiments (4 K and higher). Samples were photolyzed in the EPR cavity with the filtered, focused output (usually 307-386 nm) of a 500 W Hg arc lamp. Lamps, housings, lenses, and power supplies were obtained from Oriel Corp., Stratford, CT. Filters were obtained from Schott Optical Glass Co., Duryea, PA.

**Synthesis**

**5,5'-Di-*tert*-butyl-2,2'-Bithiophene (D.1).**[3] 2,2'-Bithiophene (0.370 g, 2.225 mmol) and *tert*-butyl chloride (1.3 g, 14 mmol) were dissolved in anhydrous methylene chloride (35 ml). Aluminum trichloride (0.52 g, 3.90 mmol) was added in one portion yielding a red solution. Stirring was continued for four hours, added to 10% HCl (45 ml) and extracted with diethyl ether. The organic layer was dried over $MgSO_4$ and concentrated. The residue was redissolved in hexanes and subjected to flash chromatography on silica gel using hexanes as an eluant. Final recrystallization from methanol afforded 380 mg (61.3%) of pure product. $^1H$ NMR ($CDCl_3$): $\delta$ = 1.38 (s, 18 H); 6.69 (d, J = 3.6 Hz, 2 H); 6.89 (d, J = 3.6 Hz, 2 H); GC/MS: 278 ($M^+$, 34); 263 (M-15, 100); 248 (23); $\lambda_{max}$ ($CH_2Cl_2$)= 316 nm.

**2-*tert*-Butyl thiophene (D.4).**[5] A solution of thiophene (19.1 g, 0.227 mol) and *tert*-butyl chloride (20 g, 0.216 mol) in methylene chloride (50 ml) was added dropwise at -78°C to a stirring suspension of aluminum chloride (30.26 g, 0.2269 mol) in anhydrous methylene chloride (100 ml). The suspension was allowed to warm to room temperature overnight yielding a brown-black solution. Stirring was continued for a further 24 hours under argon and the mixture was added to crushed ice (400 g). The aqueous layer was extracted with methylene chloride (3 x 25 ml) and the combined organic extracts were washed with water, 1% KOH solution and again with water and passed through a short plug of silica gel. Simple distillation (160-165°C) afforded 15.35 g (51%) of crude product shown by GC/MS to be a mixture of 97% mono *tert*-butyl thiophene and 3% 2,4-bis(*tert*-butyl) thiophene. $^1H$ NMR evidence suggests that the desired 2-isomer makes up 91% of the monosubstituted fraction; $^1H$ NMR ($CDCl_3$): $\delta$ = 1.38 (s, 9 H); 6.81-6.82 (m, 1 H); 6.88-6.91 (m, 1 H); 7.08-7.10 (m, 1 H); $^{13}C$ NMR ($CDCl_3$): $\delta$ = 32.59; 34.33; 121.14; 122.24; 126.30;

157.46; GC/MS: 140 ($M^+$, 27); 125 (M-15, 100); 97 (27); 85 (15).

**5-Bromo-2-*tert*-butyl thiophene (D.5).**[6] 2-*tert*-butyl thiophene **D.4** (6.349 g, 45.27 mmol) was dissolved in 1:1 chloroform-glacial acetic acid (140 ml). *N*-bromosuccinimide (8.060 g, 45.28 mmol) was added in small portions and the yellow solution brought to reflux for 15 minutes, cooled and added to water (150 ml). The layers were separated and the organic extract dried over $MgSO_4$ and concentrated. The reaction was shown to have been quantitative by GC/MS. The residue was then distilled under high vacuum (0.1 torr, 20-25°C) to yield pure product in quantitative yield; $^1H$ NMR ($CDCl_3$): $\delta$ = 1.34 (s, 9 H); 6.57 (d, J = 3.8 Hz, 1 H); 6.83 (d, 3.8 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$): $\delta$ = 32.22; 34.91; 108.59; 121.56; 129.13; 159.15; GC/MS: 220 (M-$^{81}Br$, 25); 218 (M-$^{79}Br$, 24); 205 (M-$CH_3$, 100); 177(12).

**5-*tert*-Butyl-2,2'-bithiophene (D.6).** A solution of 5-bromo-2-*tert*-butyl thiophene **D.5** (1.106 g, 5.049 mmol) in dry THF (10 ml) was added dropwise to a mixture of Mg (131 mg, 5.60 mmol) in anhydrous THF. The mixture was then refluxed for 3 hours. The Grignard solution was then added dropwise at 0°C to a mixture of 2-bromothiophene (1.68 g, 10.3 mmol) and $NiCl_2(dpp)_2$ (40 mg) in 10 ml dry diethyl ether. The mixture was allowed to warm to room temperature and refluxed under argon for one hour. The reaction mixture was stirred overnight, added to 10% v/v HCl solution, extracted with diethyl ether and concentrated. The residue was redissolved in hexane and passed through a short column of silica gel and distilled at 65°C/75 mtorr yielding 496 mg (44%) of a clear oil. $^1H$ NMR ($CDCl_3$): $\delta$ = 1.39 (s, 9 H); 6.71 (d, J = 3.7 Hz, 1 H); 6.96-6.99 (m, 3 H); 7.09 (dd, J = 1.2, 3.7 Hz, 1 H); 7.15 (dd, J = 1.2, 5.1 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$): $\delta$ = 32.37; 34.61;121.95; 122.98; 123.13; 123.73; 127.64; 134.28; 137.96; 156.89; GC/MS: 222 ($M^+$, 37); 207 (M-15, 100).

**5-Bromo-5'-*tert*-butyl-2,2' bithiophene (D.7).** 5-*tert*-Butyl-2,2'-bithiophene

(482 mg, 2.17 mmol)and *N*-bromosuccinamide (385 mg, 2.16 mmol) were dissolved in 1:1 chloroform/glacial acetic acid (15 ml) and the solution was stirred at room temperature for 2 hours. The mixture was then added to water (20 ml) and extracted with chloroform. The organic layer was washed with water, 1% KOH aqueous solution and again with water. The organic layer was then evaporated to yield a white solid which was recrystallized from methanol to afford 650 mg (99%) of pure product. mp 81-83°C; $^{1}$H NMR ($CDCl_3$): δ = 1.38 (s, 9 H); 6.82 (d, J = 3.7 Hz, 1 H); 6.71 (d, J = 3.7 Hz, 1 H); 6.90 (d, J = 3.7 Hz, 1 H); 6.93 (d, J = 3.7 Hz, 1 H); $^{13}$C NMR ($CDCl_3$): δ = 32.35; 34.68; 110.15; 122.08; 123.48; 130.48; 133.28; 139.51; 157.49; GC/MS: 302 ($M^+$, $^{81}$Br,35); 300 ($M^+$, $^{79}$Br,32); 287 (M-15, 100).

**Compound D.2.** Bisboronic ester **D.8** (202 mg, 0.546 mmol), $Pd(PPh_3)_4$ (25 mg, 4%) and 5-bromo-2-*tert*-butyl thiophene (240 mg, 1.095 mmol) were dissolved in toluene (12 ml) and the mixture purged with argon. Aqueous $Na_2CO_3$ (2 M, 2.5 ml) was added and the two-phase mixture was brought to reflux under argon for 24 hours. The mixture was then cooled, added to water (15 ml) and extracted with methylene chloride. Chromatography on silica gel using 2.5% $CHCl_3$/hexanes as eluant afforded 93 mg (41%) of product. An analytically pure sample was obtained by recrystallization from ethanol. mp 108-109°C; $^{1}$H NMR ($CDCl_3$): δ 1.38 (s, 9 H); 1.42 (s, 18 H); 6.80 (d, J = 3.7 Hz, 2 H); 7.14 (d, J = 3.7 Hz, 2 H); 7.46 (s, 2 H); 7.57 (s, 1 H); $^{13}$C NMR ($CDCl_3$): δ 31.30; 32.43; 34.63; 34.79; 120.38; 121.77; 122.14; 122.55; 134.97; 141.41; 152.12; 157.21; GC/MS: 410 (M,42); 395 (M-15,100); 190(41); 57(20).

**Compound D.3.** 5-Bromo-5'-*tert*-butyl-2,2'-bithiophene **D.7** (297 mg, 0.987 mmol), bisboronic ester **D.8** (189 mg, 0.508 mmol) and $Pd(PPh_3)_4$ (25 mg, 5%) were dissolved in toluene (10 ml) and aqueous $Na_2CO_3$ (2 M, 3 ml) was added. The mixture was purged with argon, refluxed for 66 hours and added to water

(20 ml). Diethyl ether was added and the organic layer was separated. Column chromatography on silica gel (10% $CHCl_3$/petroleum ether) yielded 155 mg (55%) of desired product. mp 146-148°C; $^1H$ NMR ($CDCl_3$): δ 1.38 (s, 9 H); 1.40 (s, 18 H); 6.74 (d, J = 3.7 Hz, 2 H); 7.02 (d, J = 3.7 Hz, 2 H); 7.08 (d, J = 3.7 Hz, 2 H); 7.25 (d, J = 3.7 Hz, 2 H); 7.50 (s, 2 H); 7.60 (t, J = 1.5 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$): δ 31.28; 32.38; 34.68; 34.86; 120.23; 122.02; 122.10; 123.06; 123.74; 123.92; 134.31; 134.56; 137.43; 142.76; 152.53; 157.01; DCI/$NH_3$: 575 (M,100); 559(17); $\lambda_{max}(CH_2Cl_2)$ = 355 nm.

**References**


(1) Davies, A. G.; Julia, L.; Yazdi, S. N. *J. Chem. Soc. Chem. Commun.* **1987**, 929.

(2) Davies, A. G.; Julia, L.; Yadzi, S. N. *J. Chem. Soc. Chem. Perkin Trans. II* **1989**, 239.

(3) Davies, A. G. *Chem. Soc. Rev.* **1993**, *22*, 299-304.

(4) Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Chem. Mater.* **1993**, *5*, 430.

(5) Belen'kii, L. I.; Yakubov, A. P. *Tetrahedron* **1984**, *13*, 2471.

(6) Kellogg, R. M.; Schaap, A. P.; Harper, E. T.; Wynberg, H. *J. Org. Chem.* **1968**, *33*, 2902.